Characterisation of the uranium leaching behaviour of low grade Vaal River ores

by

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Declaration

I, the undersigned, hereby declare that the work contained in this ~~dissertation/assignment~~/thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree. I certify that the work has been undertaken solely by the candidate, except where due acknowledgement is provided.

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Abstract

The uranium leaching behaviour of ore from three different mines in the Vaal River region, namely Kopanang, Great Noligwa and Moab Khotsong, was investigated. The aim of the work was to characterise the uranium leaching behaviour of the different ores. It involved a full mineralogical evaluation of the ore as well as determining optimum operating conditions for maximum extraction of uranium, relating the extractions to mineralogical features of the ores.

The major bulk minerals in the three Vaal River ores have been identified and consist primarily of quartz (70 – 80 %), with lesser amounts of muscovite (8 – 11 %). Moab Khotsong and Noligwa ore samples were found to be very similar, and Kopanang is different from the two ores. Kopanang ore has less pyrite, quartz, and chlorite than the other two ores, but contains more pyrophyllite. Chlorite is an acid consumer and a Fe^{2+}/Fe^{3+} producer in uranium leaching. The difference in mineralogy of the three ores definitely reflected in the reagent profiles during acid leaching of uranium, specifically acid consumption.

With regards to uranium occurrence, bulk uranium analysis showed that 80 – 90 % of the uranium in the ores is contained as uraninite, 8 – 19 % as brannerite, and the balance as traces of coffinite and uranium phosphates. Uranium grain sizes were found to be very small, with 50 % of the particles passing 19.4, 21.3 and 23.2 µm for Kopanang, Noligwa and Moab Khotsong respectively. The degree of liberation of the uranium-bearing minerals was low, between 11 and 45 %, and expectedly increased as particle size decreased. However, between 87 and 93 % of the uraninite particles and 71 to 86 % of the brannerite particles have more than 10 % of their surfaces exposed, and even higher proportions have more than 5 % of their surfaces exposed.

The primary experiments were designed within practically attainable boundaries, although special experiments were performed outside the boundaries during subsequent mechanistic studies. H_2SO_4 addition varied between 10 and 25 kg/t, temperature varied between 40 and 60°C, and MnO_2 addition varied between 2 and 4 kg/t (100 percent MnO_2). MnO_2 was added as pyrolusite, 1.5 hours after addition of acid. A relative pulp density of 1.55 was used. Leaching times of 24 and 48 hours were investigated. The ore was milled to 80 % -75 µm, even though coarser grinding was also investigated.

It was found that 60 – 90 % dissolution could be achieved as leaching conditions were varied within the operating window. Acid addition had the greatest influence on final uranium extractions. Practically useful results, within the operating window attainable in a plant, can be summarised as follows:

- Uranium dissolutions are 80 – 85 % for Great Noligwa and Moab Khotsong ores, and 85 – 90 % for Kopanang ore
- Required residence time = 24 hrs
- To achieve the above dissolutions, Kopanang ore requires at least 11 kg/t acid, while acid requirements for Great Noligwa and Moab Khotsong ores are 14 and 16 kg/t respectively
- MnO_2 addition can be kept at a minimum, because sufficient Fe can be leached from the ore (meaning only enough MnO_2 for conversion of ferrous to ferric needs to be added)
- The chlorite dissolution reaction consumes acid, generates ferric and ferrous ions, but also generates dissolved silica. Therefore, the kinetics of this reaction must be understood in order to control it to the lowest extent possible, without impairing the availability of dissolved iron.

An understanding of the factors responsible for the leaching behaviour of uranium-bearing ores is critical in achieving optimal uranium recoveries. This is particularly important in light of the fact that dissolutions higher than 90 % are very difficult to achieve under the normal operating conditions employed on the South African acid leaching plants.

While solubility limitations were initially suspected, it was found that the reason for the existence of the upper limit for dissolution was most likely due to the presence of aerially locked uranium minerals (uranium minerals that is not exposed to the leaching environment). However, residue analysis showed that most of the uraninite dissolved and that the major fraction of unleached uranium existed as brannerite which is in fact exposed to the leaching environment. Therefore, the slow leaching kinetics / intrinsic inertness of brannerite was considered as the limiting factor for not achieving optimum recoveries.

To achieve optimal extraction, considering the mineralogical characteristics of the ores (in terms of a plant's flow/operational perspective), a diagnostic leaching approach was followed. A mineralogy-leachability explanation is presented to rationalise the difficulty in exceeding 90 % dissolution from low grade uranium ores on the basis of a novel diagnostic leaching method. More specifically, to determine the interrelationship between mineralogy, mineral liberation and the leaching behaviour of uranium, a methodology was developed for unlocking uranium by a combination of chemical (drastic leaching of minerals associated with the residual uranium) and physical (fine grinding to increase area exposure and liberation) methods.

Diagnostic leaching results indicated that to improve uranium dissolution beyond 90 %, uneconomical conditions (residence time between 48 and 72 hours, constant pH = 1 or Eh = 700 mV) need to be considered and it will still not necessarily be possible to increase beyond 95%. The maximum obtained is 98% using nitric acid digestion at evaluated temperatures (90°C).

Mineralogical analysis indication that it is possible to leaching brannerite but, the leaching kinetics thereof is very slow. Based on the diagnostic leaching tests the following is recommended for the tree

ores tested: Sulphuric acid leaching must be used for treating Kopanang ore. If the brannerite concentration of Noligwa and Moab Khotsong ore is < 20 % sulphuric acid leaching is recommended but if the brannerite concentration > 20 % other leaching methods will be recommended (i.e. pressure leaching or using a different leaching reagent).

A non-linear decision tree model was developed for modelling of the experimental data and is presented in this thesis. In this context it would be more realistic to determine a range for expected recovery rather than trying to determine an exact value. Therefore, a classification tree model was used. Using this method, just evaluating the tree shows that: For uranium dissolution higher than 70% a residence time longer that 17 hours is required including an acid addition higher that 11.35 kg/t for Noligwa and Moab Khotsong ore while lower acid concentration can be tolerated for Kopanang ore. It is proven that that model can with 86% accuracy separate that into the various classes. Through cross validation it is also proven to be a representative model with an average success rate of 84 % for classification of data with a standard deviation of 2.8%. This model can be used to predict the expected dissolution range based only on the operating parameters within the Vaal River context. Since the model is based on laboratory experimental data it can not necessarily be used for plant operation/optimisation purposes. It is recommended to develop an equivalent model using pilot plant data to develop a more accurate model which can also be used for optimisation purposes.

Although it is not part of the original scope of the project (based on the information gained though out the project), a proposal of an empirical model simulator is also presented. Since development of the simulator is still in the developing stages, this thesis will only include the algorithm as well as a basic model predictor which can be used for future research. The ideal is to develop a simulator has the ability to predict uranium leaching behaviour and reagent consumption based on mineralogy.

Gold extractions obtained by forward leaching (direct cyanide leaching of gold) were compared with those obtained by reverse leaching (sulphuric acid leaching of uranium followed by cyanide leaching of gold) for three different Vaal River ores, to quantify the benefits of reverse leaching option. Reverse leaching of gold recovery by between 3 and 4 percentage points, improving total gold recovery to 98 %. A gold benefit of between 0.4 and 0.6 g/t was measured. The exact financial gain is dependant on the gold price and other economic factors, but an estimated benefit for treating an average of 240 000 t ore/month is in the order of R 14 000 000/month. The reverse leaching operation for the recovery of both gold and uranium is therefore a financially justified process route, because recovery of uranium will ensure that the costs are lower than the revenue increment.

Opsomming

Die logingsgedrag van uraan erts vanaf drie verskillende myne in the Vaalrivier omgewing, naamlik Kopanang, Noligwa en Moab Khotsong is ondersoek. Die doel van die studie is die karakteriseering van die uraan logingsgedrag en behels 'n indiepte mineralogiese evalueering van die verskillende ertse, die bepaling van die optimale bedryfskondisies vir die ekstraksie van uraan as ook die bepaling van 'n verband tussen ekstraksie en mineralogiese eienskappe van die erts.

Die grootmaat minerale van die drie Vaalrivier ertse is geidentifiseer en bestaan hoofsaaklik uit kwarts (70 - 80 %), met 'n laer konsentrasie muskoviet (8 – 11 %). Daar is gevind dat die Moab Khotsong en Noligwa erts monsters tot 'n groot mate ooreenstem, terwyl Kopanang erts daarvan verskil. Kopanang erts bevat minder piriet, kwarts en chloriet maar meer pirofilliet in vergelyking met die ander twee ertse. Chloriet is 'n suur verbruiker en 'n Fe^{2+}/Fe^{3+} verskaffer in uraan logings prosesse. Dit blyk uit die resulte dat die verskil in die mineralogie van die drie ertse definitief reflekteer op die reagense profiele tydens suur loging van uraan, veral suur verbruik.

Die grootmaatanalise, in terme van die aanwesigheid van uraan, toon dat 80 – 90 % van die uraan in die erts voorkom as uraniniet, 8 – 19 % as branneriet en die balans kom voor as koffiniet en uraan-fosfate. Daar is gevind dat die uraan korrelgrootte baie klein is, met 50 % van die partikels kleiner as 19.4, 21.3 en 23.2 µm vir Kopanang, Noligwa en Moab Khotsong respektiewelik. Die graad van bevryding van die uraan bevattende minerale was laag (tussen 11 en 45 %) en neem na verwagting toe soos partikel grootte afneem. Nietemin, tussen 87 en 93 % van die uraniniet partikels en 71 – 86 % van die branneriet partikels het meer as 10 % van die mineraal oppervlakte blootgestel aan die logings omgewing met selfs hoër proporsies met meer as 5 % blootgestelde oppervlak area.

Die primêre eksperimente was ontwerp binne die praktiese grense haalbaar op 'n aanleg. Spesiale eksperimente was wel ook uitgevoer buite die grense, vir opeenvolgende meganistiese studies. H_2SO_4 byvoeging was gevarieer tussen 10 en 25 kg/t, temperatuur gevarieer tussen 40 en 60 °C en MnO_2 byvoeging is gevarieer tussen 2 en 4 kg/t (100 persent MnO_2). MnO_2 is toegevoeg as pirolusiet 1.5 uur na die toevoeging van die suur. 'n Relatiewe pulp digtheid van 1.55 was gebruik. 'n Loging residensie tyd van 24 en 48 uur was ondersoek. Die erts was gemaal tot 80 % -75 µm alhoewel growwer maling wel ook ondersoek is.

Daar is gevind dat 60 – 90 % oplossing wel bereikbaar is binne die bedryfsgense. Dit blyk dat die suur byvoeging die grootste invloed het op die finale uraan ekstraksie. Praktiese nuttige informasie, binne die bedryfsgense van 'n aanleg, kan as volg opgesom word:

- Uraan oplossings tussen 80 – 85 % vir Great Noligwa en Moab Khotsong erts en tussen 85 - 90 % vir Kopanang erts.
- Vereiste residensietyd = 24 uur
- Om begenoemde oplossings te bereik, benodig Kopanang erts ten minste 11 kg/t suur, terwyl die suur vereistes vir Noligwa en Moab Khotsong erts 14 en 16 kg/t is onderskeidelik
- MnO_2 toevoeging kan tot 'n minimum beperk word aangesien voldoende Fe geloog word vanaf die erts (dus sleg genoeg MnO_2 vir die omskakeling van Fe^{2+} na Fe^{3+} word benodig)
- Die chloriet oplossings reaksie verbruik suur en genereer Fe^{3+} en Fe^{2+} as ook silika in oplossing. Dit is dus belangrik om die kinetika van die reaksie te verstaan om sodoende die reaksie tot 'n groot mate te onderdruk sonder om die beskikbare yster in oplossing te beinvloed

'n Deeglike begrip van die faktore verantwoordelik vir die logingskarakteristieke van uraan bevattende ertse is krities om 'n optimale uraan opbrengs te bereik. Dit is veral belangrik aangesien oplossings hoër as 90 % moeilik is om te bereik onder die normale beheer kondisies wat gebruik word op Suid Afrikaanse suurlogingsaanlegte.

Terwyl oplosbaarheidsbeperkings oorspronklik verdink was, is daar gevind dat die bestaan van 'n hoër limiet vir uraan oplosbaarheid waarskynlik 'n gevolg is van die teenwoordigheid van area geslote uraan minerale (uraan minerale wat nie aan die logings area blootgestel is nie). Nietemin, residu analiese toon dat die meeste van die uraniniet opgelos het en dat die grootste fraksie van ongeloogde uraan voorkom as brannerite, wat wel bloot gestel is aan die logings omgewing. Gebaseer op die bevindings word die stadige loging kinetika / intrisieke traagheid van brannerite gereken as die beperkende faktor vir optimum uraan herwinnig.

Om optimale ekstraksie te bereik, gelet op die mineralogiese karakteristieke van die erts (in terme van 'n aanleg se vloei / beheer perspektief), was 'n diagnostieke logingsbenadering gevolg. 'n Mineralogiese-uitloging verduideliking word bespreek om die beperking van oplossings hoër as 90 % te bespreek vir lae graad uraan ertse wat gebaseer is op 'n stap vir stap diagnostiese metode. Meer spesifiek, om die interaksie tussen die mineralogie, mineraal bevryding en logingsgedrag van uraan te bepaal is 'n metodologie ontwikkel om uraan minerale te bevry deur 'n kombinasie van chemise (drastiese loging van minerale geassosieer met die residu uraan) en fisiese (fyn maling om die area van blootstelling en bevryding van uraan minerale te vergroot) metodes.

Die diagnostiese resultate wys daarop dat om uraan oplossing te verhoog bo 90 %, onekonomiese kondisies (residensie tyd tussen 48 en 72 uur, konstante pH =1 of Eh = 700 mV) oorweeg moet word en dit nie noodwendig oplossings hoër as 95 % bewerkstellig nie. Die maksimum ekstrasie wat bereik was is 98 % tydens salpetersuur vertering by hoë temperature (90°C).

Mineralogiese analieses wys daarop dat dit wel moontlik is om branneriet te loog maar dat die loging kinetika baie stadig is. Gebaseer op die diagnostieke logings resultate word die volgende aanbeveel: Swawelsuur loging vir die behandeling van Kopanang erts. Indien die konsentrasie van branneriet in Noligwa and Moab Khotsong erts laer is as 20 % sal swawelsuur loging aanbeveel word maar indien dit verhoog (>20 %) moet ander logings tegnieke oorweeg word (bv. drukloging of die gebruik van ander logings reagense)

'n Nie linieêre besluit boom model was ontwikkel vir die modelering van die eksperimentele data en word weergegee in die tesis. Aangesien daar meer waarde lê in die bepaling van 'n verwagte uraan oplossings in 'n bepaalde gebied, eerder as om die presiese waarde te probeer bepaal is dit as 'n klassifikasie model hanteer. Deur hierdie metode te volg kan daar, gebaseer op die ontwikkelde boom die volgende afleidings gemaak word: Om oplossing bo 70% te bereik is 'n residensie tyd van langer as 17 uur benodig as ook 'n suur toevoeging van meer as 11.35 kg/t vir Noligwa en moab Khotsong erts terwyl minder suur benodig word vir Kopanang erts. Daar is getoon dat die model met 86 % akkuraatheid die data kan skei in die verskillende klasse. Kruis valideering van die model toon dat dit verteenwoordigend is en gemiddeld 84 % sukses behaal in die klassifiseering van data met 'n standard afwyking van 2.8 %. Hierdie model kan gebruik word om die verwagte oplossings gebied te voorspel gebaseer op die beheer veranderlikes binne the Vaalriver konteks. Aangesien die model gebaseer is op laboratorium gegenereerde data kan dit nie noodwendig gebruik word vir aanleg beheer doeleindes of optimiseering nie. Daar word dus aanbeveel om dieselfde model te ontwikkel vir proef aanleg data om 'n meer akkurate model te ontwikkel wat gebruik kan word vir optimiseerings doeleindes.

Alhoewel dit nie deel was van die oorspronklike omvang van die projek nie (gebaseer op die informasie versamel deur die verloop van die projek) word 'n voorstel van 'n empiriese model simulator bespreek in die tesis. Aangesien die ontwikkeling van die simulator nog in die ontwikkelings fase is sal die tesis slegs die algoritme as ook 'n basiese model voorspeller simulator insluit wat vir toekomstige navorsing gebruik kan word. Die ideaal is om 'n simulator te ontwikkel wat die vermoeë het om die uraan logingsgedrag te voorspel as ook die reagense verbruik gebaseer alleenlik op mineralogie.

Goud ekstraksies verkrygbaar deur voorwaartse loging (direkte sianide loging van goud) is vergelyk met ekstraksies verkry deur terugwaartse loging (swawelsuur loging van uraan gevolg deur sianide loging van goud) vir die drie verskillende Vaal rivier ertse. Die hoof doel is die kwantifiseering van die voordele ten opsigte van terugwaartse loging. Terugwaartse loging van gold verhoog die goud opbrengs tussen 3 en 4 persentasie punte wat lei tot 'n totale gold herwinning van 98 %. 'n Goud wins van tussen 0.4 en 0.6 g/t is bepaal. Die presiese finansieële wins is sterk afhanklik van die goud prys en ander ekonomieses faktore, maar 'n geskatte wins vir behandeling van gemiddeld 240 000 t erts/maand is in die orde van R 14 000 000/maand. Daarom is die terugwaartse logingsmetode vir die herwinnig van beide goud en uraan 'n finansieël geregverdigde proses roete.

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Chapter 1

Introduction

The uranium industry has undergone a remarkable transformation from a vital commodity for nuclear weapons to a more peaceful role as a fuel for the generation of electrical energy. Uranium deposits are found all over the world, but the decision to mine is a function of many factors including uranium grade, extraction method, market prices and social and environmental considerations. The following illustration shows that the largest uranium deposit (28% of the total world's uranium) is found in Australia while 7% is located in South Africa.

Figure 1.1: Uranium deposits over the world [www.cameco.com, 2007]

In South Africa uranium is invaluably associated with gold but the uranium content of these gold deposits is very low by Australian and Canadian standards (it averages only 0.3 kg U_3O_8/t). Based on that, uranium is mainly recovered as a by-product of gold production improving the overall economics of processing these deposits. With the drop in the uranium price in the mid 80's the production costs exceeded the uranium price and the main benefit from uranium leaching (as a by-product) was in the extra unlocking of gold. Therefore, the exploration in the uranium industry (to improve the uranium recovery process) in that period of time was minor but the current increasing interest in nuclear technology as well as the increase in the uranium price is prompting the uranium mining industry to re-evaluate their uranium recovery strategies.

The scientific objective of the project was to obtain a better understanding of the uranium leaching behaviour of ore from three different AngloGold Ashanti mines: Kopanang, Noligwa and Moab Khotsong starting with a detail mineralogical evaluation of the three different ores. This understanding was delivered in the form of a mineralogy-leachability explanation as well as a diagnostic leaching tool. Standard and diagnostic leaching tests were performed to generate the necessary data. As part of the objectives, the benefits of a reverse leach operation are quantified.

The deliverables of the project are a report including:

- Detailed mineralogical characterisation of the ore from Kopanang, Moab Khotsong and Noligwa Mines
- Description of relationships between the properties of the uranium deposits and their behaviour during leaching
- A diagnostic method that can be used to characterise the ease with which various uranium fractions can be leached in a given ore
- An analysis of forward- and reverse- leach options
- A statistical model that is able to predict expected uranium dissolution within the Vaal River context
- A proposed leaching algorithm/model that can be used to predict optimum reagent dosages and maximum obtainable extractions, based on the mineralogy properties of the ores determined by the diagnostic leach/mineralogical examinations

The project developed over 6 phases which are covered in detail in the following chapters. For the duration of the project there was close interaction between Anglo Research and Stellenbosch University and test work was performed at both institutions. Phase A entails the review of the classical literature which was a ongoing process throughout the entire project. During this literature survey it was found that uranium research went through phases with relative little research done especially during the 80's early 90's leaving definite scope for research in this field. The reason therefore is mostly attributed to the variation in the uranium market as well as the negative associated with uranium in that period of time. All the relevant uranium leaching literature and technology available up

to date is discussed in **CHAPTER 2** focussing on uranium in South Africa, specifically the Witwatersrand Basin.

Mineralogy of the matrix material is one of the major factors that determine which steps are necessary in order to obtain optimal results in terms of extraction, purity and costs. Phase B covered the detailed mineralogical characterisation of the ore from Kopanang, Moab Khotsong and Great Noligwa Mines in the Vaal River area which were done by the expertise of Anglo Research. In **CHAPTER 3** the results are presented specifically focussing on the uranium mineralogy including liberation, surface area exposure, particles size distribution and mineral associations. This information is critical to be able to fully understand the leaching behaviour of uranium minerals under specified conditions.

The main focus of this project was sulphuric atmospheric acid leaching. The question may arise why this specific method? The motivation therefore lay in the fact that AngloGold Ashanti already has a sulphuric acid uranium leaching plant in operation. This justifies the reason for determining the maximum extraction using this specific method before looking into alternative techniques for example pressure leaching. Moreover, this information will also contribute to the economical analysis evaluating various methods comparing uranium recovery, operating as well as capital costs for future uranium operation development within the Vaal River area.

Phase C involved the evaluation of uranium recovery within plant operation boundaries. The standard leaching experiments were done in collaboration with the Anglo Research team. Examining the nature of the uranium-bearing minerals, laboratory tests were done under controlled conditions, so that the effect of both leaching conditions and mineralogical compositions (3 different ore types) could be determined. A factorial design developed for this purpose include the variation of: acid concentration(9.9 kg/t, 12.8 kg/t, 16.3 kg/t), temperature (40 °C, 50 °C, 60 °C) as well as oxidant concentration(2 kg/t, 3 kg/t, 4 kg/t). The oxidant, pyrolusite is used which contains both MnO_2 and FeO thus; indirectly the ratio of Fe^{3+}/Fe^{2+} is changed. The process variables including uranium dissolution were monitored as a function of time for each ore type and combination of leaching conditions. These experiments address all possibilities for reaching a specific maximum yield which are discussed in detail in **CHAPTER 4**. All analyses (liquid and solid samples) were done by Anglo Research.

As mentioned, uranium is being recovered as a by-product of the gold production. One of the main problems that are limiting optimum recoveries in gold extraction is the fact that gold is captured within gangue minerals rendering it inaccessible to the leaching environment. It is known that leaching uranium before leaching gold liberate more gold, increasing the overall gold yield. In Phase D the effect of forward and reverse leaching on the recovery of gold is evaluated for the three different ores to quantify the benefit of reverse leaching in terms of gold extraction. These tests were done at Anglo Research and the results are presented in **CHAPTER 5.**

In terms of a plant's flow/operational perspective an important consideration is to establish the deportment of uranium within the ore. Phase E involves the development of a diagnostic leaching tool.

The ideal is to develop a step-by-step method that can be followed to evaluate and fully characterise any uranium containing ore body within the Witwatersrand Basin. This information will be essential regarding choice of leaching technique, operating conditions and expected uranium recovery. It will also lead to a better understanding of the leaching fundamentals of the specific ore treated. In **CHAPTER 4** standard leaching results indicate that it is that the optimum yield of ± 90 % are obtained even moving outside the plant operation boundaries. A diagnostic leaching approach was followed to rationalise the difficulty in exceeding 90 % dissolution from low grade Vaal River uranium ores. More specifically, as described in **CHAPTER 6** the interrelationship between mineralogy, mineral liberation and the leaching behaviour of uranium were determined. The methodology was based on unlocking uranium by a combination of chemical (drastic leaching of minerals associated with the residual uranium) and physical (fine grinding to increase area exposure and liberation) methods. The analyses of the diagnostic leaching tests were done by the Geology Department at the University of Stellenbosch while the mineralogical analyses were completed by the Geology Department at the University of Johannesburg.

In **CHAPTER 7** the data generated are modelled using decision trees to statistically predict the expected uranium recovery within the boundaries tested. This model assists in terms of optimisation of the extraction process. The ultimate aim is to develop a uranium simulator that has the ability to predict uranium leaching behaviour and reagent consumption based on mineralogy and reaction rates of the various minerals. Although it is not part of the original scope of the project (based on the information gained though out the project), a proposal of an empirical model simulator is presented and is still in the development stages. The proposed model did not include an in-depth study into the kinetics of the various minerals or interaction between different species and will only to suitable as first approximation for future modelling of reaction kinetics of the uranium leaching system. The thinking behind the model as well as the assumptions made is discussed in **CHAPTER 7.** To address the concerns about laboratory scale it will be proposed to do some experimental work on plant scale or to include plant data in future research.

Chapter 2

Uranium Technology Review

Electricity consumption worldwide has been growing rapidly since the early 1980's and the electricity demand is soon expected to exceed the supply capacity. Nuclear technology may be the solution to the problem due to its availability and large energy potential. The recent implementation of the Kyoto Protocol, (which demands a reduction of CO_2 emissions, a by-product of coal-fired electricity generation) gives nuclear technology even a more positive outlook. Using uranium, substantially more energy can be produced without emitting CO_2, making it more environmentally friendly as well as reducing the world's dependency on fossil fuel resources.

Hence, uranium is back on the radar. This chapter gives a brief overview of the uranium history, the uranium market, and the current status of uranium in South Africa as well as processing operation opportunities. It includes an in-depth review on uranium leaching technology currently available, which cover leaching chemistry, leaching kinetics, diagnostic leaching and forward and reverse leaching. Previous modelling work done on leaching circuits is also being reviewed. The Witwatersrand Basin, specifically the Vaal River region, is the main focus in this review.

2.1 Uranium Overview

Uranium was discovered by the German chemist, Martin Heinrich Klaproth in 1789 and was named after the planet Uranus. It is a dense (an SG of 18.7), silver grey metal which is highly radioactive. Uranium was first isolated as a metal in 1841 by Eugene-Melchior Peligot and in 1896 a French physicist Henri Becquerel discovered radioactive properties within uranium minerals. Before the advent of nuclear energy, uranium had very limited uses and was primarily used as salts to colour glass and ceramics [Wikipedia, 2007].

Uranium is one of the most abundant elements found in the earth's crust. Although it is widely disseminated in nature, varying from 2 – 4 ppm, concentrations of uranium vary according to the substances it is mixed with. Concentrated uranium ores are found in just a few places, usually in hard rock or sandstone. Table 2.1 shows known conventional resources of uranium.

Table 2.1: Known conventional resources of uranium [www.xemplar.ca, 2007]

High-grade ore body - 20% U	200,000 ppm* U
Low-grade ore body - 0.1% U	1,000 ppm U
Granite	4 ppm U
Sedimentary rock	2 ppm U
Average in earth's continental crust	1.4 ppm U
Seawater	0.003 ppm U
*ppm = parts per million	

Uranium is a very concentrated source of energy, but is not directly usable for power generation. The most abundant uranium isotope is U_{92}^{238} which forms 99.275% of natural uranium, while the fissible isotope U_{92}^{235} only contributes 0.7 %. For generation of electricity in nuclear reactors a concentration higher than 3.5% U_{92}^{235} is required. To put it in prospective, explosion (bomb) grade uranium has a U_{92}^{235} concentration of some 90 %. The enrichment process removes U_{92}^{238} isotopes producing a higher U_{92}^{235} isotope concentration.

The basis for nuclear power is Einstein's formula $E = mc^2$, where c represents the speed of light. Inside a nuclear reactor when the nucleus of an U_{92}^{235} atom captures a neutron it splits to form Ba_{56}^{144} (Barium) and Kr_{36}^{89} (Krypton). This process, called fission, initiates the nuclear mass defect, where the mass after fission is a fraction lower than the original mass. In this process two or three additional neutrons are also thrown off. If these neutrons cause the nuclei of other U_{92}^{235} atom to split a fission 'chain reaction' can be achieved [Wikipedia, 2007]. From Einstein's formula it is clear that even a small mass difference will release large amounts of energy. Table 2.2 compares the energy production of various energy sources.

Table 2.2: Energy product by different energy sources [www.xemplar.ca, 2007]

ENERGY SOURCE	ELECTRICITY PRODUCED
1 kg of firewood	1 kwh (kilowatt hour)
1 kg of coal	3 kwh
1 kg of oil	4 kwh
1 kg of Uranium	**50,000 kwh**

Nuclear energy offers a clean and efficient alternative to energy produced from coal, oil or natural gas and today approximately 17 % of the world's electricity is generated from nuclear reactors which are comparable to world demand in 1960 (see Figure 2.1). In 2005 a total of 440 commercial nuclear reactors were operating world wide. At present there are 24 reactors under construction, 41 planned (which is approved and funded) and another 113 proposed.

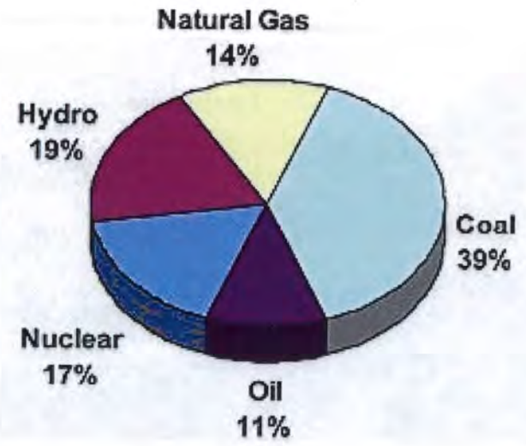

Figure 2.1: World electricity generation [www.xemplar.ca, 2007]

The basic sequence of steps in the nuclear fuel cycle:

- Extraction of uranium from the ores to produce U_3O_8
- Conversion of U_3O_8 to gaseous UF_6
- Enrichment of U^{235} to fissionable concentrations
- Fabrication of UO_2 fuel pellets from UF_6
- Utilisation of the nuclear fuel
- Storage / re-processing of spent fuel
- Final permanent disposal of nuclear waste

From 1985 the uranium market was driven by liquidation because of very large utility inventories forcing many mines world wide to close down. Exploration of the uranium mining industry in this period was minor. For many years primary uranium production was not enough for world reactor requirements. The remainder was provided by secondary sources, such as utility inventory, dismounting military weapons and reprocessing spent fuel. With decreasing secondary supplies and increasing reactor requirements, shortages of uranium are expected. It is therefore inevitable that the demand for mined uranium will grow. The predicted supply and demand forecast is presented in Figure 2.2.

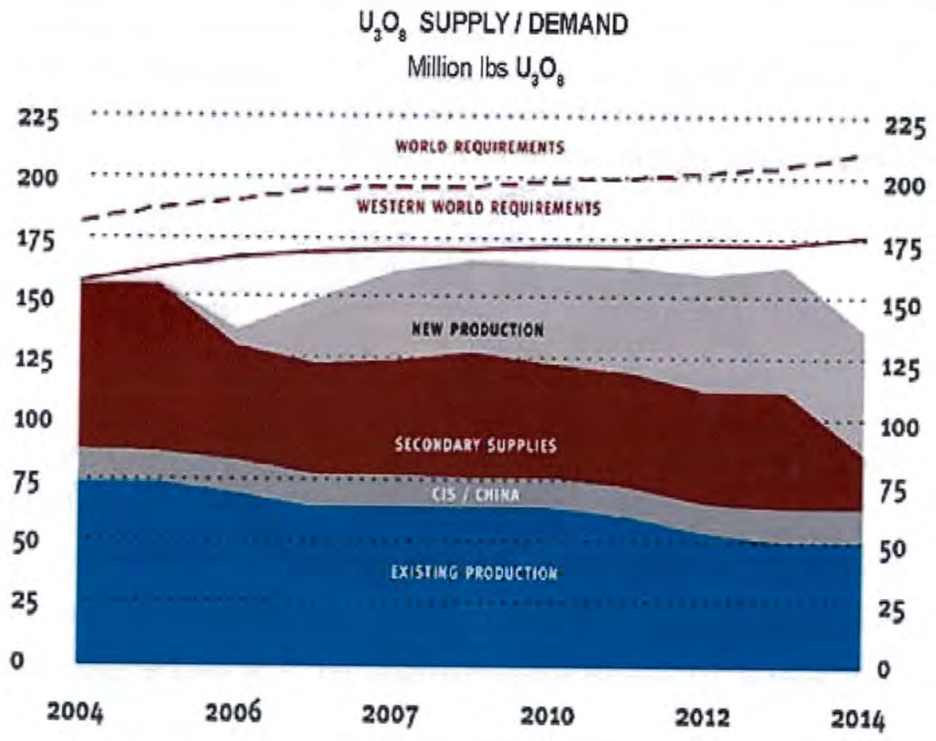

Figure 2.2: Supply and demand of uranium [www.xemplar.ca, 2007]

Despite the urgent need for additional mined uranium, there are still some challenges to be met. The most challenging is time constraints on new sources of mined uranium which mainly involve technical, economic, regulatory and environmental implications associated with new mining developments. Currently nuclear power is seen as one of the only acceptable long term solutions to wide-scale reduction in greenhouse gasses and rapid increasing electricity demand. This realisation resulted in an exponential increase in the uranium price since 2003 (as illustrated in Figure 2.3). It is against this supply and demand graph (Figure 2.2) that some analysts have forecast a uranium price of some $200 per pound in the next few years. This promising outlook has prompted the uranium mining industry to rethink their strategies.

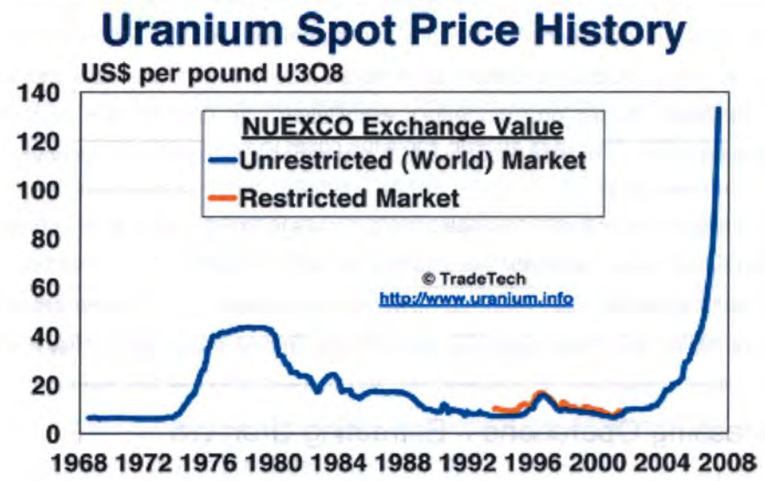

Figure 2.3: NUEXCO / TradeTech Uranium Spot History chart [Ickes and Finch, 2007 – www.stockinterview.com]

2.2 Uranium Mineralogy in the Witwatersrand Basin

The first comprehensive study on the uranium mineralisation of the Witwatersrand sediments was done by Liebenberg from 1947 [Liebenberg, 1955]. As indicated by many authors, uraninite and brannerite-type minerals ($U_{1-x}Ti_{2+x}O_6$) are the main uranium carriers in the Witwatersrand ores. Coffinite ($(U,Th)SiO_4$) is of relative importance only in the West Rand Goldfields and the uranium contribution from uraniferous zircon ($ZrSiO_4$) is negligible [Smit, 1984; Ford and Gould, 1994].

Uraninite contains uranium as an oxide, approximately of the formula UO_2, but always shows a degree of oxidation, therefore the composition is generally given as UO_{2+x}. Thus, the composition of most natural uraninite falls in the range of $UO_{2.04}$ to $UO_{2.07}$ [Gupta and Singh, 2003]. Uraninite has a density of 11 000 kg/m^3 and the range of grain size is narrow, being 250 µm with an average of 75 µm [Smit, 1984]. Pitchblende ($U_2O_5.UO_3$) is a common variation of uraninite and more or less amorphous, generally having the composition between UO_2 and UO_3. The ratio is usually greater than 1 [Gupta and Singh, 2003]. Tetravalent uranium has a low solubility in both diluted acid and carbonate solutions while hexavalent uranium is readily soluble in acid media. To achieve economic recovery, oxidation to the hexavalent state is essential.

Brannerite, as commonly referred to, is a uranium titanate (with x=0) and one of the important uranium-bearing minerals in the Witwatersrand ores, especially in the Vaal Reefs area. It is not readily liberated during crushing and has a lower rate of dissolution. Brannerite usually occur as a microcrystalline phase (compacted and in discrete grains), similar to uraninite. Moreover, its refractory properties are due to its titanium content as well as its intimate association with host minerals, which

are usually secondary constituents of the ore and somewhat poorly crystallized [Bovey, 1973]. As brannerite is frequently enclosed in these host minerals it becomes inaccessible until the host minerals are partially dissolved. Based on brannerite's association with silicates and leucoxene (mixture of ilmenite and rutile) it can be divided roughly into 2 categories [Glatthaar and Duchovny, 1979]:

- Brannerite associated with silicates usually occurs in minute, compacted crystals intergrown in siliceous materials. Due to the enclosure of siliceous materials, it is refractory.
- Brannerite associated with leucoxene which is referred to as uraniferous leucoxene for the sake of distinction. The structure is more loosely knitted, thus more readily dissolved.

2.3 Processing Operations – Extracting Uranium

The type of uranium mineralisation and the nature of its association within a particular deposit have a major impact on the process route selection. Conventional processing of uranium ores begins with crushing and grinding to produce a product suitable for further processing. Primary extraction of uranium from the ore begins with the leaching step (alkaline or acid). The uranium in solution is separated from the solid residue by a series of solid-liquid separation and optionally ion-exchange steps. The solution is further purified and concentrated by solvent extraction. Ammonia diuranate [$(NH_4)_2U_2O_7$], the final product from primary mine production, is precipitated from concentrated uranium solutions using NH_3 gas. Other forms of 'yellow cake' can be precipitated by using different precipitating agents. NH_3 is then removed by intensive drying and calcination to produce the oxide, U_3O_8.

The most expensive and critical unit operation in uranium extraction is the leaching step, which will be discussed in more detail. The efficiency of uranium leaching controls the economic viability of treating low grade deposits and is mostly sensitive to ore characteristics.

2.3.1 Acid or Alkaline Uranium Leaching

The uranyl ion is highly soluble in acidic or carbonate-bicarbonate solutions and forms stable complexes with both carbonate and sulphate ions [Merritt, 1971]. The choice of leaching procedure (acid or alkaline leaching) and operating parameters depends on the physical characteristics of the ore such as the type of uranium mineralisation, degree of liberation as well as the nature of constituent gangue minerals present.

Due to the nature of the ores in South Africa, acid leaching is common practice. Alkaline leaching is mainly used in the treatment of ores with a high carbonate mineral content. This is due to their high acid consumption. The amount of carbonate minerals present in South African ores does not necessitate the use of less effective and more complex carbonate leaching. Advantages of acid leaching include lower grinding requirements, shorter leaching times, lower leaching temperatures and more flexibility regarding ore variability [James and Simonsen, 1978].

2.3.2 Leaching Techniques

A range of techniques are employed for acid leaching. The techniques frequently used are: (i) "In situ" leaching, which refers to the application of leach solutions directly to the ore body; (ii) Dump and heap leaching, which is the treatment of mined material that has received little or no size reduction following removal from the ore body. Heap leaching is used for oxide-bearing minerals, while dump leaching refers to leaching of sulphide-bearing minerals; (iii) Percolation leaching, a technique where the leach solution is percolated through crushed ore (particle size 5-20 mm) and bedded into vats or tanks; (iv) Agitated leaching involves the leaching of fine particles (<200µm), where the solids are dispersed in the liquid (which contains the leaching medium) by gas injection of mechanical agitation to improve the rate of reaction; and (v) Pressure leaching is done without the addition of any reagent except oxygen at elevated temperature and pressure [Hayes, 2003].

Methods (i) and (ii) entails leaching by means of perculation (liquid added to solids), which are popular for treating extreme amounts of ore. Methods (iii) and (iv) involve crushing solids into small pieces before being contacted with solvents (solids added to liquid). Agitated leaching (method iv) and pressure leaching (method v) are popular leaching methods when an especially high recovery rate can economically justify the typically higher operating cost (e.g. gold extraction) [Hayes, 2003]. Figure 2.4 summarises the uranium leaching technology available, and locations of where it is mostly employed.

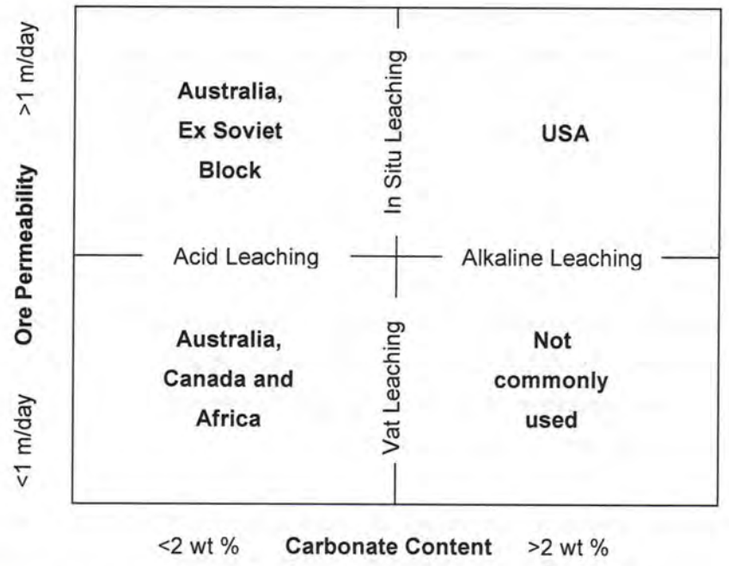

Figure 2.4: Summary of the uranium leaching technology available

Two leaching methods can be considered when dealing with the recovery of uranium for low grade ores: Agitated atmospheric sulphuric acid leaching and more aggressive pressure leaching. For agitated atmospheric sulphuric acid leaching, reactants (acid as well as an oxidant) are needed at

elevated temperature. Pressure leaching of uranium ores (which contain sulfidic minerals) may be leached without the addition of any reagents, except oxygen, by treatment at elevated temperature and pressure. Results obtained by Merritt [1971], for South African ores, showed an 85 % uranium extraction for conventional leaching methods while 90 % uranium extraction was obtained using pressure leaching. Pressure leaching was not in the scope of this study, thus the focus will be on conventional agitated leaching (to determine the maximum extraction to be expected using ore from the Vaal River Region) before considering more aggressive leaching methods (e.g. pressure leaching).

Leaching, as practiced in Vaal River plants, is accomplished by oxidation of the insoluble U^{4+} form to the acid-soluble U^{6+} form in an acidic environment (H_2SO_4), using ferric as an oxidant. To maintain reasonable reaction rates, depleted Fe^{2+} is continually converted to Fe^{3+} using pyrolusite (MnO_2-rich ore). The ferric/ferrous couple serves as an electron transfer catalyst between the solid oxidant (MnO_2) and UO_2. The electrochemical nature of the uranium leaching process therefore means it is confined to a specific Eh-pH window.

2.4 Uranium Leaching

2.4.1 Basic Chemistry of Uranium Acid Leaching

For agitated atmospheric sulphuric leaching of uranium ore, uranium bearing minerals can be divided into different leaching sections, depending on leaching response. Ford and Gould [1994] divided it into 4 categories: fast, medium, slow and non-leaching uranium. The fast leaching fraction refers to uranium in the U^{6+} state and requires an acidic environment to be soluble, hence the fast leaching response.

$$UO_3 + 2H^+ \leftrightarrow UO_2^{2+} + H_2O \qquad [2.1]$$

The medium leaching fraction refers to the tetravalent uranium which has a low solubility in dilute acid. Witwatersrand ore mostly consist of uraninite which is uranium in the U^{4+} state. In practice, to achieve economic recovery, the application of an oxidising agent is essential to induce minerals containing tetravalent uranium to react and be taken into solution.

Nicol proved that this reaction occur though an electro-chemical mechanism [Nicol *et al.*, 1975]. Uraninite (UO_2) acid-leaching is accomplished by oxidation of the insoluble U^{4+} form to the acid-soluble U^{6+} form in an acidic environment (H_2SO_4), using Fe^{3+} since the addition of a oxidant such as manganese dioxide is not sufficient in itself to achieve the change of valency. The following reactions are limited within a specific Eh-pH window (see Figure 2.5).

Half-cell reactions: $UO_2 \leftrightarrow UO_2^{2+} + 2e^-$ [2.2]

$2Fe^{3+} + 2e^- \leftrightarrow 2Fe^{2+}$ [2.3]

Overall reaction: $UO_2 + 2Fe^{3+} \leftrightarrow UO_2^{2+} + 2Fe^{2+}$ [2.4]

To maintain reasonable reaction rates, depleted Fe^{2+} is continually converted to Fe^{3+} using pyrolusite (MnO_2-rich ore), i.e:

$$2Fe^{2+} + MnO_2 + 4H^+ \leftrightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O \qquad [2.5]$$

Potential can either be controlled via concentration or selection of lixiviant and or oxidant, or rather a combination thereof. Selection of the type of lixiviant requires economical as well as practical considerations. In South Africa, sulfuric acid is used because it is readily available and can be produced on site, as the ores contain sufficient amounts of pyrite. An important advantage of using sulfuric acid is that anionic ion exchanger resins, used to absorb the uranium, is more selective for uranium than cationic type exchangers, which are used after HNO_3 and HCl leaching [Merritt, 1971]. According to Merritt [1971], stable sulphate-complexes form during acid leaching:

$$UO_2^{2+} + SO_4^{2+} \leftrightarrow UO_2SO_4 \qquad [2.6]$$

$$UO_2SO_4 + SO_4^{2-} \leftrightarrow [UO_2(SO_4)_2]^{2-} \qquad [2.7]$$

$$[UO_2(SO_4)_2]^{2-} + SO_4^{2-} \leftrightarrow [UO_2(SO_4)_3]^{4-} \qquad [2.8]$$

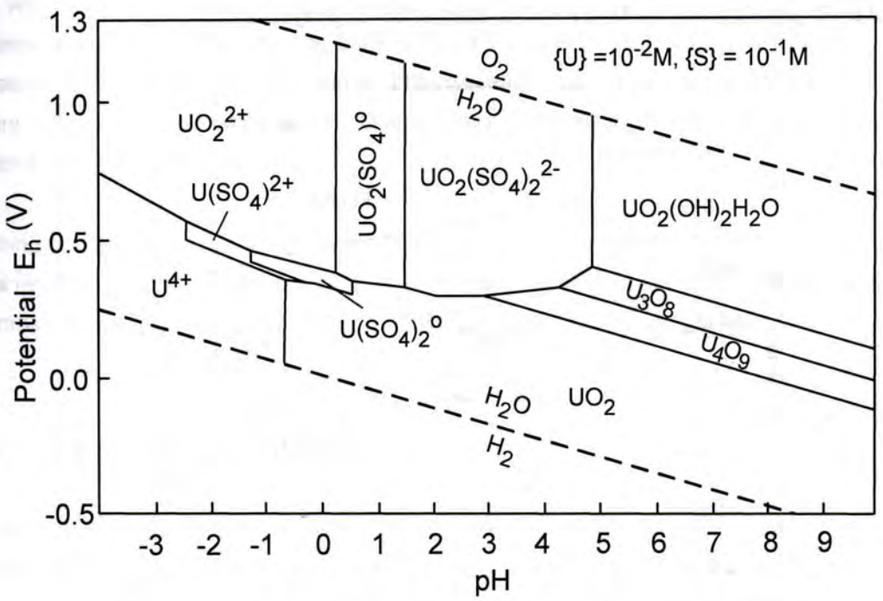

Figure 2.5: Eh-pH diagram U-S-H_2O system at 25°C [Hayes, 2003]

The region of stability of the oxides is much smaller in the absence of sulphate. Thus, the presence of these ions during leaching increases the driving force of the leaching reaction, independently of the influence of pH. However, the bisulfate ion has a greater affinity for the resin in the CCIX (anionic exchanger) compared to the sulfate, resulting in higher recoveries. In uranium leaching it is not only necessary for the uranium ion species to be stable, but also the reactant species Mn^{2+}, Fe^{3+} and Fe^{2+} species. The Eh/pH diagrams for both are presented in Figure 2.6 and Figure 2.7.

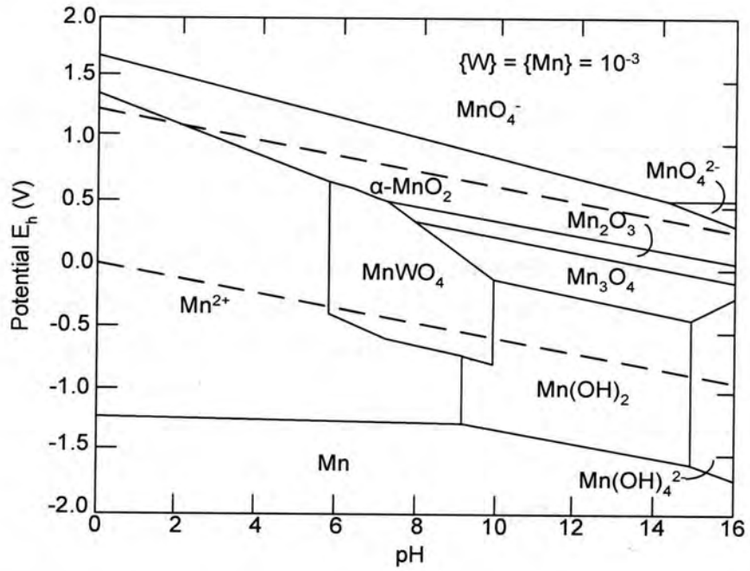

Figure 2.6: Eh-pH diagram of a Mn-W-H_2O system at 25°C, [Hayes, 2003]

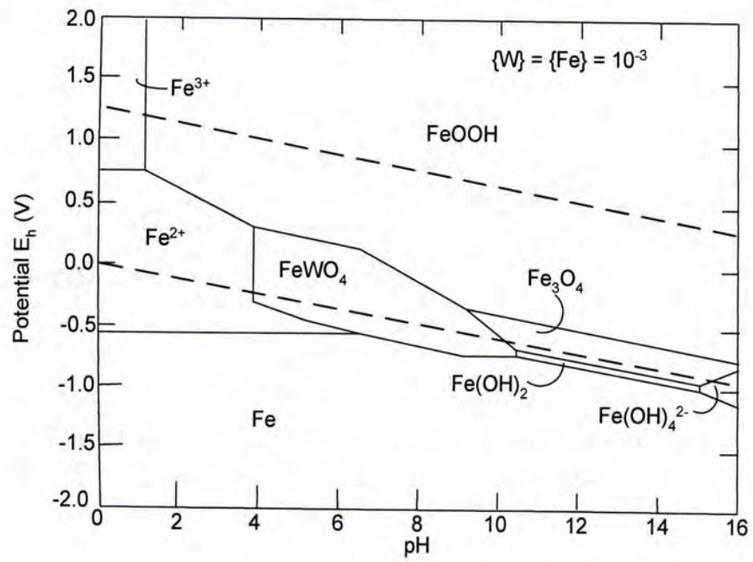

Figure 2.7: Eh-pH diagram of a Fe-W-H_2O system at 25°C, [Hayes, 2003]

Some uranium minerals are intrinsically inert or frequently enclosed in the host gangue minerals, which renders it inaccessible. These fractions are referred to as the slow and/or non leaching fractions. Ford and Gould [1994] found that the amount of inert uranium is, in absolute terms, fairly similar for all Witwatersrand ores, at about 0.015 kg/t to 0.030 kg/t.

Gangue minerals are also a great concern during leaching since non-selective leaching causes many species, besides uranium, to be leached. The presence of UO_2^{2+} chelating ions as well as reductants (e.g. carbonaceous matter, H_2S, etc.) are of great concern. Carbonaceous matter not only acts as a reductant, but along with certain clays, may function as an ion exchanger to absorb uranium from the solution. According to a study done by Ford and Gould [1994] on ore from the Vaal River South Mine, the variations in the non-leaching fractions were attributed to the variation in the head grade as it was thought that the absolute amount of inert uranium was a fixed amount. Preferential dissolution of uranium needs careful optimisation of acid levels, time, potential, temperature, degree of liberation and particle size.

2.4.2 Key Parameters in Uranium Acid Leaching

2.4.2.1 Acid Concentration

Acid is necessary in the leaching process to create the right environment to transfer uranium into the aqueous phase ($U^{4+} \rightarrow U^{6+}$). The key factor of the acid concentration is to maintain a free acid concentration (FA) sufficient to attack the uranium minerals without dissolving an excess amount of gangue materials. In the presence of carbonated gangue minerals it is important to neutralize it first, since it will react before the uranium minerals. Acid consumption is a function of the gangue constituents present in the ore, referring back to the importance of mineralogy. Carbonate minerals is the biggest acid consumers. Uraninite and pitchblende leach at a pH between 1.5 and 2, while apatite is not very reactive if the pH exceeds 1.5. Quartz, which is the major component, is unreactive under conventional acid leaching conditions.

For leaching of uraninite a FA of 3-7g/l is necessary, while for leaching of brannerite and davidite a FA >50g/L is required [Gupta and Singh, 2003]. The acid concentration at the end of the leaching process is of utmost importance, since a change in the pH may lead to precipitation of uranium (see [2.9]).

$$UO_2SO_4 + 3H_2O \leftrightarrow UO_2(OH)_2H_2O + H_2SO_4 \qquad [2.9]$$

Strong acids are strong electrolytes, which are assumed to ionize completely in water. Most of the strong acids are inorganic acids: hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClPO_4$) and sulphuric acid (H_2SO_4). Note that sulphuric acid is a diprotic acid. When calculating the pH value it is important not to assume a unity activity factor when determining the correlation between sulphuric acid and the actual pH since the activity factor influences the pH [Chang, 1998] see equation [2.10].

Table 2.3 shows the pH ranges at which various cations may precipitate uranium from sulphate solutions.

$$pH = -\log(\gamma [H^+]) = -\log\gamma - \log[H^+] \quad [2.10]$$

Table 2.3: pH range at which various cations may precipitate uranium [Bonthuys and Mhulungu, 2005]

Cation	pH Range			
	Hydroxide	Phosphate	Arsenate	Carbonate
	OH^-	PO_4^-		CO^{2-}
Uranyl	3.8 – 6.0	1.9 – 2.5	1.3 – 1.7	3.5 – 6.0
Uranous	2.5 – 6.0	<1.2	<1.2	-

Some mineral acids, for instance nitric acid (0.96 V vs SHE) or Caro's acid (H_2SO_5) (1.81V vs SHE), can serve as both acid and oxidant [Haque and Ritcey, 1982].

2.4.2.2 Oxidant Addition

For uranium to enter the aqueous phase the uranium must leave the solid lattice. Through an electrochemical process, minerals containing U^{4+} is transformed to U^{6+} and then taken into solution. The addition of an oxidizing agent induces this process. The potential needed is in accordance with the Nernst equation [2.11].

$$E = E^o + \frac{RT}{nF} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad [2.11]$$

In a Butler-Volmer formalism, the overpotential affects the reaction rate exponentially. Therefore, the influence of the absolute Fe^{3+}/Fe^{2+} ratio (controlled by solid oxidant addition and reactivity of Fe-bearing ore constituents) on the rate will be linear. Potential is a function of temperature and the ferric ferrous ratio and can be determined via the Nernst equation. A satisfactory redox prediction was obtained by Ring [1980] using the following equation [2.12]:

$$E = 397 + 0.1984T \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \quad [2.12]$$

The choice of oxidant is a factor of both oxidation potential and cost. Pyrolusite is mostly used in the mining industry since it is inexpensive and converts Fe^{2+} to Fe^{3+} at lower temperatures and acid concentrations compared to other oxidants (Table 2.4). The ferric/ferrous couple serve as an electron transfer catalyst between the solid oxidant (MnO_2) and UO_2. The elementary reactions are:

$$UO_2 \leftrightarrow UO_2^{2+} + 2e^- \qquad E^0 = -0.39 \text{ V vs SHE} \quad [2.13]$$

$$2Fe^{3+} + 2e^- \leftrightarrow 2Fe^{2+} \qquad E^0 = +0.77 \text{ V vs SHE} \quad [2.14]$$

$$MnO_2 + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O \qquad E^0 = +1.23 \text{ V vs SHE} \quad [2.15]$$

Note that while MnO_2 can in principle, oxidise UO_2 directly, the reaction would be too slow as it would require direct contact between two naturally separate solid phases. Therefore, in practice, MnO_2 oxidises Fe^{2+} to Fe^{3+} and Fe^{3+} oxidises UO_2 to UO_2^{2+}.

Table 2.4: Oxidation potentials of oxidants [Haque and Ritcey, 1982]

Oxidant	Potential (V) vs SHE
MnO_2	1.2
$Fe_2(SO_4)_3$	0.77
Cl_2	1.35
H_2O_2	1.77
$NaClO_3$	1.45
Caro's Acid	1.81
HNO_3	0.96
O_3	2.07
$K_2Cr_2O_7$	1.33
$KMnO_4$	1.49
O_2	1.22
$KHSO_5$(ozone)	1.44

According to Merritt [1971], a satisfactory level of oxidizing conditions is usually obtained in a leached slurry with an oxidation/reduction potential between -400 and -500 millivolts (vs SCE – Standard Calomel Electrode Potential). Studies showed that the rate of dissolution do not correspond to the standard redox potentials of the oxidants used. Thus, it is reasonable to say that the rate of oxidation of U^{4+} in solid UO_2 is NOT controlled solely by the thermodynamic driving force provided by the difference between the value of the equilibrium potential for the half cell reactions [Burkin, 2001]

2.4.2.3 Temperature

Temperature plays a big part in reaction kinetics; in fact, temperature and time is interdependent of each other. By rearranging the rate law equation it can be seen that there is a linear dependency between temperature and the rate of the reaction. Thus, an increase in temperature will either reduce the reaction time required or increase the percentage extraction. This will lead to an increase in the capacity of the equipment.

The disadvantages of high temperature leaching are: (i) an increase in acid and oxidant consumption, (ii) chemical response of gangue minerals as well as (iii) corrosion. Usually it is more economical to provide a maximum amount of time for the leaching procedure and to keep the temperatures as close as practical to ambient conditions. Due to these disadvantages many uranium leach circuits are usually operated at temperatures not exceeding 60ºC. Temperature is usually controlled in acid leaching circuits by means of direct steam injection. Additional heat is obtained through heat of solution of sulphuric acid. Where the acid addition is high, it may be desirable to add the acid in stages to avoid localised high temperatures [Merritt,1971].

2.4.2.4 Residence Time

A typical residence time used in the uranium leaching industry is 24 hours. Residence time not only has a economical implication, but can also lead to down stream problems since longer residence times lead to increases in the SiO_2 levels. Dissolved silica foul the resin and cause significant drops in the adsorption rates in the counter current ion exchange (CCIX) following the counter current decantation section (CCD).

2.4.2.5 Grinding

Grinding is important as it liberates the minerals of interest so that it can be exposed to the lixiviant. Particle size influences the degree of liberation and the degree of reaction. Finer sizes are characterised by the following: (i) high surface areas for reaction,(ii) shorter reaction times, as well as (iii) having the advantage of an more manageable slurry suspension.

On the other hand, it is also associated with an increase in cost as well as an increase in viscosity, thus having an adverse affect on leaching. If the ore is grinded too fine the density and viscosity will be too high, which will decrease the contact time and result in a lower extraction. It is of utmost importance to find an optimum between particle size fractions, degree of liberation, density and viscosity. High viscosity will also cause problems with diffusion, plus cause problems with the settling process separating solids from liquid. However, grinding is optimised in terms of the process of gold production, since it is much more sensitive to the particle sizes due to very low ppm levels.

2.4.2.6 Agitation Speed

In practice there are two methods of agitation, a mechanical or pneumatic method. The pneumatic method of agitation is mostly used with either compressed air or high pressure steam (if heating is necessary). The reason is low initial costs, as well as low maintenance costs (no moving parts). This mechanism of agitation provides the additional benefit of aerating the solution. Pneumatically agitated leaching vessels in the industry are referred to as pachuca tanks.

It is possible to eliminate external mass transfer if the agitation is great enough. During the leaching of minerals from ores, reactions typically occur in a product layer that forms around the unreacted core. As agitation is increased the effective thickness of the product layer is minimised adjacent to the solid surface. Figure 2.8 illustrates the effect of stirring on the dissolution of solids. Either excessive viscosity or poor agitation will cause the leaching rate to be diffusion controlled instead of reaction controlled, resulting in slower leaching rates.

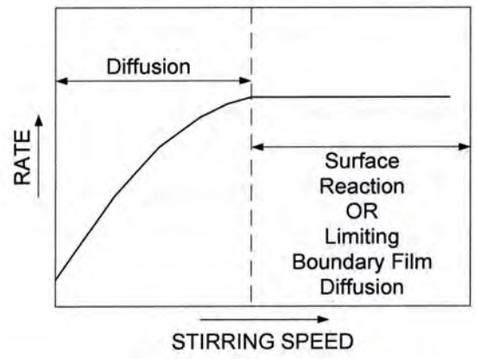

Figure 2.8: Rate of reaction as related to stirring speed [Sohn and Wadsworth, 1979]

2.4.2.7 Pulp Density

During the leaching process the optimum density is the maximum possible density that still permits sufficient fluidity in the pulp. A dilute pulp will require additional capacity as well as sufficiently higher concentrations of reactants in solution. This may lead to lower dissolution rates or even cause re-precipitation. On the other hand, fewer reagents (acid & oxidant) are required. Thus, there is a trade off and in practice a 60:40 solid to liquid ratio is used.

2.4.3 Kinetics of different uranium and gangue minerals

Leaching in general refers to the removal of a substance from a solid via a liquid extraction media. A leaching (solid/liquid) reaction can be described as follows [2.16]:

$$A_{liquid} + bB_{solid} = cC_{liquid} + dD_{solid} \qquad [2.16]$$

The overall reaction process transferring the desired product from the solid to the liquid, involves various stages: (i) fluid phase mass transfer includes external mass transfer between the reactants in the solution and the external surface of the particle; (ii) diffusion refers to the mass diffusion though the pores of the particles to the mineral of interest; and (iii) the chemical reaction is between the mineral of interest and the reactants in solution.

The leaching rate will be determined by the step with the slowest rate. This rate controlling step can change with reaction conditions. It is important to note that individual reaction steps also interact which each other, thus is it important to consider the effect of each step in expressing the overall rate. In addition to the steps involving the chemical change of species, there are two other processes that might also have a significant influence on the overall rate, i.e. heat transfer and changes in the structure of the solids during the reaction. Solid-fluid reactions either consume or generate heat. Heat transfer involves: (i) convection/radiation between solid and surroundings and (ii) conduction in the solid. Various rate laws are proposed in literature and are summarised in Table 2.5.

Table 2.5: Summary of the rate laws proposed in literature for various possible reactions [Vetter et al., 1989 and Ford and Gould, 1994]

Reaction	Rate Law	k	E_a
$2Fe_2^{2+}+MnO_2+4H^+=2Fe^{3+}+Mn^{2+}+2H_2O$	$k[Fe^{2+}][MnO_2]$	0.025	0
$UO_2 + 2Fe^{3+} = UO_2^{2+} + 2Fe^{2+}$	$k[e^{-E_a/RT}][UO_2][Fe^{3+}]^{0.5}[Fe^{2+}]^{-0.5}$	$18x10^4$	61300
$UO_3 + 2H^+ = UO_2^{2+} + H_2O$	$k[e^{-E_a/RT}][UO_3][H^+]^2$	$6x10^{-8}$	61300
UO_2 non leaching	0		
$O_2+4H^++4Fe^{2+}=2H_2O+4Fe^{3+}$	$k[Fe^{2+}]^2$, $k= k'pO_2$	$2.2x10^{-3}$	0
$2H^++Mg_2Fe(OH)_6=2Mg^{2+}+Fe^{2+}+6H_2O$	$k[H^+]^2[Mg_2Fe(OH)_6]$	$4x10^{-5}$	0
$FeS_2+14Fe^{3+}+8H_2O=15Fe^{2+}+2SO_4^{2-}+16H^+$	$-e^{(18.41)}\left[\frac{Fe^{3+}}{Fe^{2+}}\right]^{0.41}[H_2SO_4]^{-0.57}[e^{-E_a/RT}]$		-66700
$Mg_2Fe_2Al_{3.3}Si_{2.5}°_{10}(OH)_8+4H_2SO_4=2Mg^{2+}+1.7Fe^{2+}+0.3Fe^{3+}+3.3Al^{3+}+4SO_4^{2-}+2.5SiO_4^{2-}+8H_2O$	$-e^{(-4.60)}[H_2SO_4]^{1.04}[e^{-E_a/RT}]$		-6000
$3Fe(SO_4)_3+14H_2O=2(H_3O)Fe_3(SO_4)_2(OH)_6+5H_2SO_4$	$e^{(0.70)}[Fe^{3+}]^{0.25}[e^{-E_a/RT}]$		-14600

2.4.4 Uranium Leaching in the Witwatersrand Basin

Gold deposits in South Africa are invariably associated with uranium bearing minerals. Although the uranium content of these ores is generally low by international standards, averaging around 0.3 kg U_3O_8 per ton, the overall economics of processing these deposits can be substantially improved by recovery of uranium as by-product. Moreover, the current high uranium prices as well as increased demand due to renewed interest in nuclear power provide significant incentives for dedicated uranium production.

Exploration of uranium resources in South Africa started in the late 1940s. South Africa has an estimated recoverable uranium resource of 350,000 tons. Up till 1965, South Africa operated 26 mines within the Witwatersrand Basin [http://www.sipri.org, 2007]. The oil crisis in the seventies triggered extensive exploration of uranium, leading to the country's first primary uranium mine, Beisa, which was commissioned in 1982. However, uranium was still mainly a by-product of extensive gold mining. By 1985, the number of uranium mines had decreased to 15 [Ford and Gould, 1994]. The down scaling was mostly due to the low uranium price, as well as the negative association with uranium in the eighties.

Currently, South Africa has one operating uranium recovery plant left. That is the Vaal River Operation plant in Orkney, owned by AngloGold Ashanti, which opened in 1977 and is able to produce up to 1,270 tons per year. A second facility, the Dominion Mine near Klerksdorp, owned by SXR Uranium One, is still under development and will be commissioned end of 2007 or early 2008 [http://www.sipri.org, 2007]. When fully operational, the mine is expected to produce up to 3,390 tons per year. Table 2.6 summarises uranium deposits ownership in South Africa, while Figure 2.9 shows the major uranium deposits in South-Africa. Ford and Gould [1994] evaluated the uranium plants between 1981 and 1985 and a summary of the plant conditions and results obtained are given in Table 2.7. From these results it can be seen that the dissolutions from various ores in the Witwatersrand Basin vary roughly between 70 and 90%.

Table 2.6: Uranium deposits Ownership [Wise Uranium Project, 2007]

Mine/Deposit	Ownership	Comments
Hartebeestfontein/Buffelsfontein	70%Simmer&Jack Mines Ltd 30% First Uranium Corp.	Under ground: Size: 3178 tonnes U Grade: 0.018 % U (2005) Tailingsdam: Size: 5731 tonnes U Grade: 0.008% U (2007)
Randfontein, Gauteng	Ezulwini Mining Company Pty Ltd	Size: 1495 tonnes U Grade: 0.061 % U (2007)
Karoo Basin – Beaufort West Deposit	UraMin Inc.	Size: 23 000 tonnes U Grade: 0.08%
Palabora	Palabora Mining Co Ltd	Uranium recovery plant shut down August 2001
Springbok Flats Deposit	UraMin Inc.	Size: 18 000 tonnes U Grade: 0.06-0.1%
Vaal River Area	AngloGold Ashanti Ltd	
Western Area	Western Areas Gold Mining Co Ltd	Uranium recovery plant shut down in 1998
Rietkuil, Rhenosterhoek, Bonanza South and Dominion deposits (Klerksdorp Area)	Aflease Gold and Uranium Resources (SXR Uranium One)	Size: 143 000 tonnes U Grade: 0.037%
Ryst Kuil Uranium Project	UraMin Inc.	Size: 30385 tonnes U
Denny Dalton Uranium/Gold Project	Acclaim Exploration NL	Size: 9350 tonnes U Grade: 0.03%
Harmony tailings project	Uranium One Inc.	
Mintails West Rand tailings project	Mintails Ltd.	Size: 1345 tonnes U Grade: 0.0074 % U (2007)

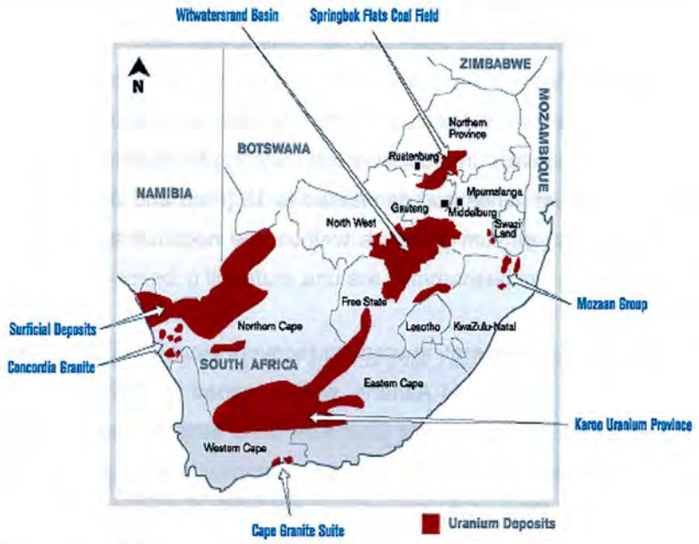

Figure 2.9: Uranium deposits in South-Africa [www.uranium1.com, 2006]

Table 2.7: Uranium plant leaching parameters in various Witwatersrand plant received between 1981 and 1985 [Ford and Gould, 1994]

Plant	Head Grade (kg/t)	U3O8 (%)	Time (h)	Temp (°C)	Ferric (g/L)	Acid (g/L)	Acid (kg/t)	MnO2 (kg/t)	Grind (%-75um)
Beisa	0.537	89	17	38-52	0.7-.0	2.4-3.3	28.2	7.7	70
Blyvoor	0.152	74	30	ambient	3.7-4.7	.2-.3	16.6	2.6	67
Blyvoor	0.204	85	31	ambient	2.8-3.	1.7-2.3	15.6	0	79
Buffels	0.291	70	21	57-66	3.7-9.5	4.9-6.4	43.3	0	74
Chemwes	0.166	81	25	45-58	0.6-0.7	2.4-3.3	13.4	1.4	70
Ergo	0.36	79	26	42			51	0	95
Harmony	0.118	65	12	ambient	2.5	3.2-11.0	16	2.1	63
Harties	0.15	75	10	58-71	1.2-2.2	3.2-3.8	14.1	2.6	65
Harties	0.163	80	14	49-71	1.1-2.2	3.3-4.3	14.1	2.6	62
Harties	1.472	89	17	72	3.6	25.0-46.5	14.1	2.6	98
M'spruit	0.13	71	16	40-70	1.8-2.5	5.0-6.0	19.5	0	56
PB(JMS)	0.098	77	25	ambient	0.8-0.9	4.5-5.7	12.9	0	48
PB(JMS)	0.667	89	59	45-60	1.7-2.1	25.7-28.9	30.1	0	70
REGM	0.276	83	11	55-60	0.7-1.3	8.7-14.5	21.8	4.5	64
VREast	0.276	81	22	54	9-3.3	4.0-7.0	22.9	2.7	70
VRSouth	0.325	73	18	51-55	0.6-1.6	3.1-6.1	24.5	4	73
VRWest	0.194	78	17	45-55	1.0-1.9	4.5-11.0	28	3.4	66
Virginia	0.134	66	18	32-40	2.6-4.5	3.4-4.8	13.5	0	62
Virgina	0.654	93	12	65	15.0-18.0	60.0-65.0	13.5	0	
WAGM	0.13	91	22	60-65	0.6-1.0	6.5-11.8	30	4	69
WDL	0.124	73	20	45-65	1.0-2.5	1.8-4.5	30.7	4.2	72
Wdrie	0.135	73	23	46-55	1.3-1.6	2.3-3.0	27.6	3.3	80
Wdrie	0.643	94	30	37	1.6-2.1	2.6-5.1	27.6	0	
WRCons	0.304	88	11	51-55	5.1-7.3	5.3-11.0	24.9	5.2	63

2.5 Diagnostic Leaching

Diagnostic leaching is typically used to characterise the leaching behaviour of a specific mineral. It is used to describe limitations in achieving 100 % recovery and conditions to overcome these limitations. The aim of diagnostic leaching is mainly to get a better understanding of the leaching fundamentals to possibly improve which then can be used to improve flow sheets.

An understanding of the factors responsible for the leaching behaviour of uranium-bearing ores is critical in achieving optimal uranium recoveries. This is particularly important in light of the fact that dissolutions higher than 90 % are very difficult to achieve under the normal operating conditions employed on the South African acid leaching plants, as seen in literature (refer to Table 2.6).

Considering optimal uranium extraction in terms of a plant's flow/operational perspective, an important consideration is the mineralogical characteristics of the ores. Typically a diagnostic leaching approach can be followed to get a much clearer view on the deportment of the specific mineral concerned. Diagnostic leaching is an analytical method developed in 1986 by Anglo American Research Laboratories (AR), originally for gold leaching [Lorenzen, 1995]. It involves a series of sequential leaches, developed to elucidate the deportment of a specific mineral within various matrices. The differences in the kinetic and thermodynamic stability of various minerals allow leach selectivity. It is therefore possible to eliminate the least stable mineral present in the ore matrix (into an aqueous media) through selective oxidative leaching. The measured concentration of the mineral of interest will represent the amount associated with specific constituent minerals. Based on this information problem areas can be identified in plants and unit operations. The first step in developing this method will be to determine the mineralogy of the ore investigated and then to design the diagnostic leaching sequence accordingly.

This mineralogy-leachability explanation can be used to rationalize the difficulty in optimizing uranium dissolution from low grade uranium ores. More specifically, to determine the interrelationship between mineralogy (mineral liberation and the leaching behaviour of uranium) a methodology can be developed for unlocking uranium by a combination of chemical (drastic leaching of minerals associated with the residual uranium) and physical (fine grinding to increase area exposure and liberation) methods. The findings from these investigations will form the guidelines for developing economically viable flow sheets for improved uranium recovery.

2.6 Forward and Reverse Leaching

As mentioned, gold in the Witwatersrand ores is usually associated with uranium. The process used for extracting gold differs from the process for the extraction of uranium. With respect to gold, two

process routes can be considered: Forward leaching (direct cyanide leaching of gold) and reverse leaching (sulphuric acid leaching of uranium followed by cyanide leaching of gold).

Both gold and uranium dissolutions from ore are electrochemical processes. As illustrated in Section 2.4.1, a pH of less than 2 and a potential between 400 and 500 mV (vs. SCE) are required for uranium leaching. The Eh-pH diagram for the Au-H_2O system is shown in Figure 2.10. It is clear that leaching uranium and gold simultaneously will be impossible in the absence of a strong lixiviant, since gold is very stable over a wide range of potential and pH values.

Gold leaching thus requires the addition of a suitable complex ligand to make leaching thermodynamically feasible in water. In industry cyanide is typically used as a lixiviant. The gold cyanide complex, $Au(CN)_2^-$, is quite stable in water (see Figure 2.11) and thus renders Au highly mobile in solution. The addition of cyanide reduces the required oxidation potential for the Au dissolution so that oxygen may be used as an oxidant at ambient conditions [Hayes, 2003]. Figure 2.10 shows that as pH increases, the maximum chemical driving force for gold leaching is reached at pH = 9.3. The reaction for the dissolution of gold in aerated cyanide solutions, originally written down by Elsner in 1846, is:

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O = 4\,Au(CN)_2^- + 4\,OH^- \qquad [2.17]$$

The cyanide process is controversial due to the highly poisonous nature of cyanide. The most toxic form of cyanide is hydrogen cyanide (HCN), either in gaseous or aqueous state. The stability of cyanide complexes is pH dependant and lime addition is required to control the pH at a sufficiently high level to avoid the volatilisation of HCN. To ensure that cyanide does not exist as HCN, leaching must be performed at more alkaline conditions, thus a pH of over 10.5 is typically maintained in industrial practice. Cyanide is very reactive and although the affinity of cyanide for gold is such that it extracts Au preferentially, cyanide also reacts with gangue minerals. The presence of gangue minerals not only leads to operational and environmental concerns, but it may also lead to resistance to cyanide treatment, since some of the gold is enclosed in the gangue and thus prevents access to the gold (called refractory gold). Gold in the Witwatersrand depository is associated with a number of different minerals and can usually be divided into the following classes [Annandale, 1995]:

1. Free Gold
2. Gold associated with pyrite
3. Gold associated with other base metal sulphides
4. Gold associated with carbonaceous matter
5. Gold associated with silicates
6. Gold associated with uranium mineralisation

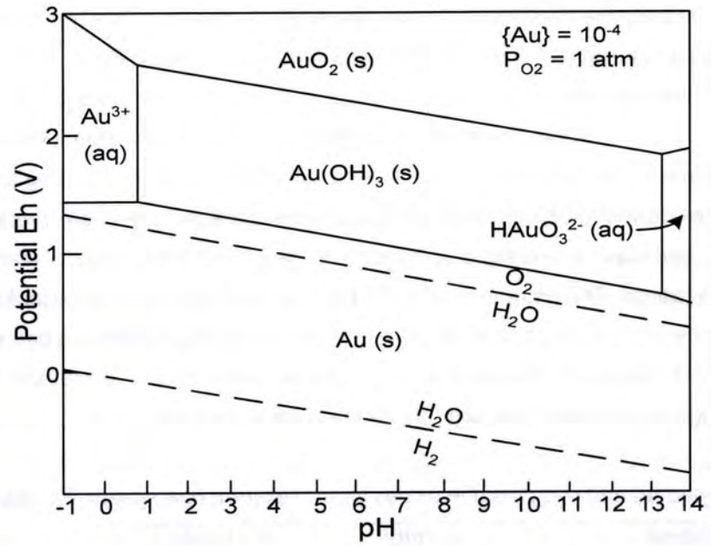

Figure 2.10: Eh-pH diagrams for a Au-H2O system [Hayes, 2003]

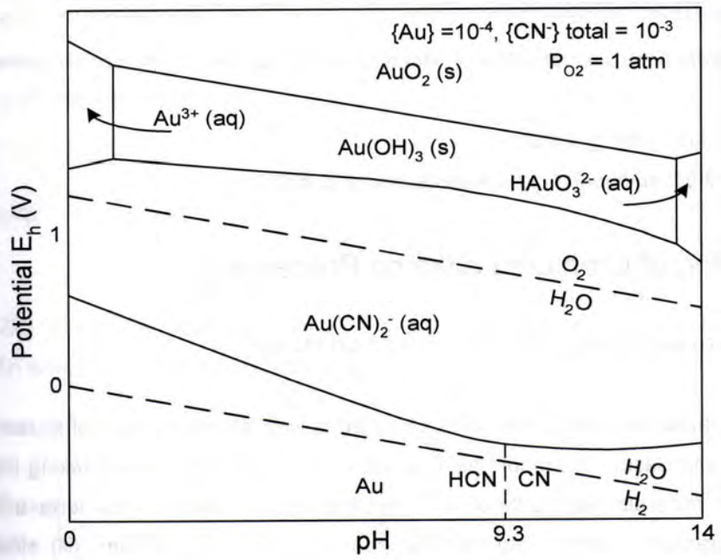

Figure 2.11: Eh-pH diagrams for a Au-CN-H system [Hayes, 2003]

Although gold is generally insoluble in acid solutions (Figure 2.10 – absence of suitable ligands, e.g. Cl^-, is assumed), through pre-acid treatment it is possible to destroy some gangue minerals, liberating gold associated with the destructed minerals, without actually dissolving the gold. It is generally known that leaching uranium before gold liberates more gold, improving the gold recovery [Lurie, 1959].

In an attempt to quantify the benefits of reverse leaching, Barnes *et al.* [1976] investigated different flow sheets involving flotation (F), gold cyanidation (G) and uranium leaching (U). Since flotation is not part of the scope, the effect thereof was not investigated. From the work done by Barnes *et al.* [1976] (indicated in Table 2.8) the F-U-G flow sheet appears to be most adequate but it may not be the most attractive choice from a practical point of view. Care must also be taken in choosing a flocculent, since it directly influences downstream processes. Previous experience indicates that reverse leach benefits may be lost if the acid leach is preceded by flotation, since a large percentage of uranium do not float and are still in the tailings. Therefore, two leaching trains will be required to account for the uranium in the tailings and different leaching conditions will need to be specified for the two processes. However, by only evaluating forward and reverse leaching a definite benefit can be realised in terms of gold extraction by doing sulphuric acid leaching (uranium) before cyanidation (gold).

Table 2.8: Combined Au and U_3O_8 residue values for the different flow sheets [Barnes et al., 1976][1]

Flow sheet	Au (g/t)[2]	U_3O_8 (g/t)[3]
G-U-F (Forward Leaching)	0.57 (0.28)	41 (27)
U-G-F(Reverse Leaching)	0.27 (0.14)	43 (35)
F-U-G (Bulk Float)	0.31 (0.15)	37 (18)

[1] Values in brackets are combined final residues assuming gold and uranium recoveries of 85% from final calcine.

[2] Rolling bottle cyanidation @ 25°C

[3] Head grade 353 g/t, sulphuric acid – ferric leaching @ 65°C

2.7 Modelling of Uranium Leaching Processes

2.7.1 The Ford and Gould uranium dissolution model

Ford and Gould based their model on data generated during laboratory tests of sixteen different ores in the Witwatersrand Basin. The model also includes a mineralogical aspect, taking into account that different uranium minerals react differently. Therefore, they created a four term uranium leaching model dividing uranium minerals into four categories: (i) fast, (ii) medium, (iii) slow and (iv) non leaching (fraction not accessible to leaching) [Ford and Gould, 1994].

MODEL: $y = f_1 \exp(-k_1F_1t) + f_2 \exp(-k_2F_2t) + f_3 \exp(-k_3F_3t) + f_4$ [2.18]

Where y is a fraction of uranium dissolved in time (t); f_1, f_2, f_3 and f_4 are the fast leaching, medium leaching, slow leaching and non-leaching fraction respectively; k_1, k_2 and k_3 are the leaching rate constants; F_1, F_2 and F_3 are a function of process conditions described in the following equation:

$$F = \left(\frac{Fe^{3+}[g/L]}{3}\right)^a \left(\frac{H_2SO_4[g/L]}{4}\right)^b \frac{\exp\left(\frac{-E}{RT[K]}\right)}{\exp\left(\frac{-E}{333R}\right)} \quad [2.19]$$

The following constants were derived using empirical fitting methods: k_1 = 11.94, k_2 = 1.14, k_3 = 0.109, a = 0.71, b = 0.64, E = 62.3 kJ/mol. For Vaal River ore Ford and Gould [1994] determined that the uranium dissolution is as follows: fast leaching (53.6%), medium leaching (18.3%), slow leaching (17.2%) and non leaching (inert) (10.9%).

This model indicates that the uranium leaching rate is dependent on the Fe^{3+} concentration rather than the Fe^{3+}/Fe^{2+} concentration ratio. This means that the overall potential is not as critical compared to the Fe^{3+} concentration. Based on this model, additional Fe^{3+} will increase uranium dissolution as well as acid concentration and temperature.

2.7.2 The Macnaughton *et al.* uranium dissolution model

Macnaughton *et al.* [1999] followed the same approach as Ford and Gould [1994], assuming that the uranium feed can be devided into four fractions (see section 2.7.1). They described the fractional dissolution (α) of uranium as a function of time:

$$\alpha = 1 - \sum_1^4 f_i \exp\left(-k_i\left([potential]^a[H^+]^b \exp\left(\frac{-E_a}{RT}\right)\right)t\right) \quad [2.20]$$

In equation [2.20], potential is measured in (mV), the acid concentration H^+ in (g/L) and E_a in (J/mol. K) is a constant. An empirical model was fitted using experimental data from Olympic Dam ores to give:

$$\alpha = 1 - \begin{pmatrix} 0.685\exp\left[-2.36x10^9[H^+]^{0.96} t\exp\left(\frac{-66700}{RT}\right)\right] \\ +0.098\exp\left[-9.09x10^{-11}(potential)^{6..32} t\exp\left(\frac{-66700}{RT}\right)\right] \\ +0.118\exp\left[-9.86x10^{-10}[H^+]^{0.96} t\exp\left(\frac{-66700}{RT}\right)\right] \\ +0.099 \end{pmatrix} \quad [2.21]$$

Compared to the activation energy determined by Nicol *et al.* [1975], the predicted activation energy is in the same range. Since this model is develop using a specific ore it can not be applied to other ore types. Developing a similar model by including the mineralogical data, instead of using experimental

data to empirically determine f_i could prove beneficial. The mineralogical data can be determined on the basis of a mineralogical examination or using a diagnostic leaching method.

2.8 Summary

This chapter provides a sound background in the field of uranium extraction more specifically uranium leaching focussing on the Witwatersrand Basin. The recent power crisis in South Africa has encouraged the industry to investigate new ways to generate electricity. Nuclear energy seems to be the answer for long-term, sustainable and clean energy. Very little research in the uranium field has been done since the mid eighties, but renewed interest in nuclear energy is putting more focus on uranium. There are still concerns to be addressed, such as long-term waste disposal, high capital costs, the public's acceptance, safety concerns (especially in the light of Chernobyl and Three Mine Island) as well as concerns regarding terrorist attacks. Leaching forms an integral part in recovering uranium from ore bodies, since it determines the economic viability of the treatment of uranium deposits. After a thorough literature survey the following hypothesis can be formulated:

In the Witwatersrand Basin, acid leaching is mostly employed due to the mineralogy of the ore body. The uranium leaching process is of electrochemical nature and therefore can be optimised in terms of acid concentration, potential, temperature and time, but it is critical to include the mineralogy of the ore. It appears that the absolute quantity of unleachable uranium in the Witwatersrand ores is within a defined range. The maximum extractions (as a percentage) at a given set of conditions will depend primarily on the head grades and the approach of the uranium in solution to the solubility limit. With regards to the mineralogy-dissolution relationships, it is expected that fully liberated uraninite will be *fast* leaching (complete dissolution in less than 2 hrs), while partially liberated uraninite will correspond to what is conventionally called *medium* leaching uranium in the modelling literature. Although there is still some uncertainty regarding the solubility of brannerite, it is speculated that fully liberated brannerite will be *slow* leaching, while unliberated brannerite will be inert. Coffinite is not expected in significant amounts in the Vaal River ores that will be used in this study. The mineralogical study will determine both the deportment of U-bearing minerals to the various size fractions, as well as the percentage surface area exposure of the minerals. Diagnostic leaching of uranium will most likely involve the following steps: aggressive leaching (max plant conditions), drastic leaching (higher temperature and reagent levels) and then nitric acid leaching that will most probably remove the remaining uranium. A diagnostic leaching approach can be followed to rationalize the leaching behaviour and to design the uranium leaching process accordingly. Regarding the forward leaching vs. reverse leaching options, it is common knowledge that leaching of uranium liberates more gold. This study will simply quantify this benefit for three Vaal River ores.

Various uranium leaching models have been developed in the past but have limited usage since it can only be used in specific boundaries. The ideal is to develop a more robust model, where only the mineralogy of a specific ore deposit will be necessary to predict the recovery of uranium on the basis of the reaction kinetics of the different mineral species.

Chapter 3

Uranium Mineralogy

In South Africa, specifically the Witwatersrand Basin, uranium is found in quartz pebble conglomerates [Merritt, 1971]. The mineralisation thereof is understood to comprise of (in order of significance): quartz (SiO_2), pyrophyllite ($AlSi_2O_5OH$), muscovite ($KAl_2(Si_3Al))_4O_{10}(OH)_8$), paragonite ($NaAl_2(Si_3Al)O_{10}(OH)_4$), pyrite ($FeS_2$), chlorite ((Fe, Mg, Al)$_6$(Si, Al)$_4O_{10}(OH)_8$) and chloritiod ((Fe, Mg, Mn)$_2Al_4Si_2O_{10}(OH)_4$) [Smit, 1984]. The less common constituents are titanium oxides, chromite, zircon, sulpharsenides, sulphides, uranium minerals, uraniferous carbon, gold and PGM minerals [Smit, 1984].

Uranium is found in over 200 different minerals, but the most common uranium minerals found in economic deposits are uraninite (uranium oxide), pitchblende (uranium oxide-massive variety of uraninite), coffinite (uranium silicate), brannerite (uranium titanate), carnotite (uranyl vanadate), yuyamunite (uranyl vanadate) and uranophane (uranyl silicate) [British Geological Survey, 2005].

The type of uranium mineralisation and the nature of its association within a particular deposit have a major impact on the process route selection. Mineralogy is the key to a better understanding regarding processing of uranium, specifically leaching, since it directly influences leaching performance. This chapter gives an overview of the current AngloGold Ashanti uranium operations including flow sheets. It also introduces the general mineralogy of the Witwatersrand ore, focusing on the bulk mineralogy of ore from three different Vaal River mines: Kopanang, Noligwa and Moab Khotsong.

3.1 Background

The three AngloGold Ashanti mines Kopanang, Noligwa and Moab Khotsong are located in the northern part of the Free State, next to the Vaal River near Orkney. The mines exploit the Vaal Reefs at depths varying between 1300-2200m, 1500-2800m and 2100-3700m for the three mines respectively, below surface. Presented in Figure 3.1 is a map of the Vaal River area indicating the locations of the mines.

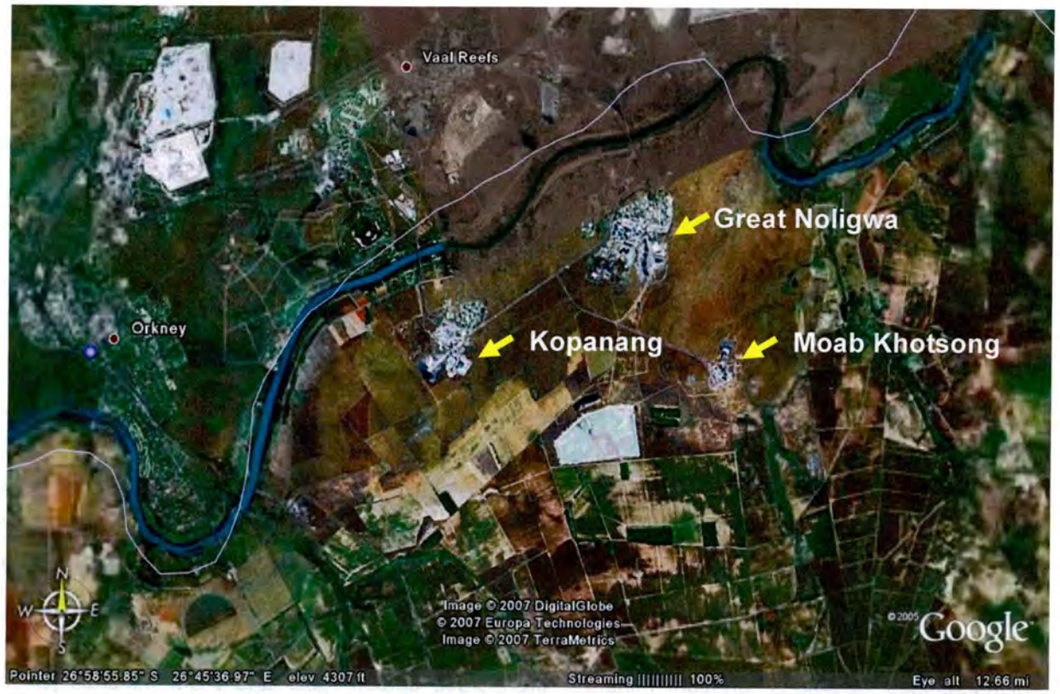

Figure 3.1: Area map of the Vaal River Region [Google Earth]

3.2 Current AngloGold Ashanti uranium operations

Currently only ore from Noligwa Gold Mine are treated for uranium extraction. Reverse leaching is used, extracting uranium before gold. The ore is firstly crushed and milled to approximately 70 – 75 % -75µm and sent to the uranium plant for sulphuric acid leaching to remove the uranium which is then sent back to gold extraction. Figure 3.2 is a schematic diagram of the process flow at the AngloGold Ashanti's South Uranium Plant.

The slurry received from Noligwa Gold Plant is sent to the leaching section were it is treated with H_2SO_4, MnO_2 and steam to dissolve the uranium into solution using 10 pachucca tanks. Oxidising sulphuric acid leaching is carried out at a temperature above ambient (40–80 °C). This leads to non-selective leaching, causing many species besides uranium being leached. The presence of these anionic species can cause problems in uranium extraction.

The dissolved uranium is then washed using solid-liquid separation in 5 counter current decantation (CCD) thickeners. The pregnant solution, containing the uranium, leaves the CCD to go to the Counter Current Ion Exchange (CCIX) section and the solids are pumped back to Noligwa Gold for further gold leaching. The CCIX is principally an ion exchange process using Amber Jet 4400 CL resin and sulphuric acid. In the CCIX the uranium is stripped from the pregnant solution in the absorption columns selectively and loaded onto the resin. The resin is then stripped and the uranium is loaded on

the eluant using 5 elution columns and sulphuric acid. The solution leaving the elution columns is called the eluate. This is a semi batch process. The CCIX reduce the volume from approximately 1000 m^3/h to 30 m^3/h.

The eluate is then pumped to the Solvent Extraction section (SX) where most of the impurities are removed using extraction, scrubbing and stripping processes. The aqueous phase with uranium leaving the solvent extraction section is known as OK Liquor which is processed further in the Ammonium diuranate (ADU) process. The solution received from the SX section contains uranium in its phosphate form, $(NH_4)_2UO_2(SO_4)_2$. NH_3 gas is used to precipitate the uranium as Ammonium diuranate. In this section impurities like SO_4^{2-} which are added in the stripping section, are removed.

$$2UO_2SO_4 + 6NH_4OH \rightarrow (NH_4)_2U_2O_7(s) + 2(NH_4)_2SO_4 + 3H_2O \quad [3.1]$$

The product from the ADU section, $(NH_4)_2U_2O_7$, is then sent to Nufcor. Nufcor is providing a service to the mine by further processing it to uranium oxide (U_3O_8).

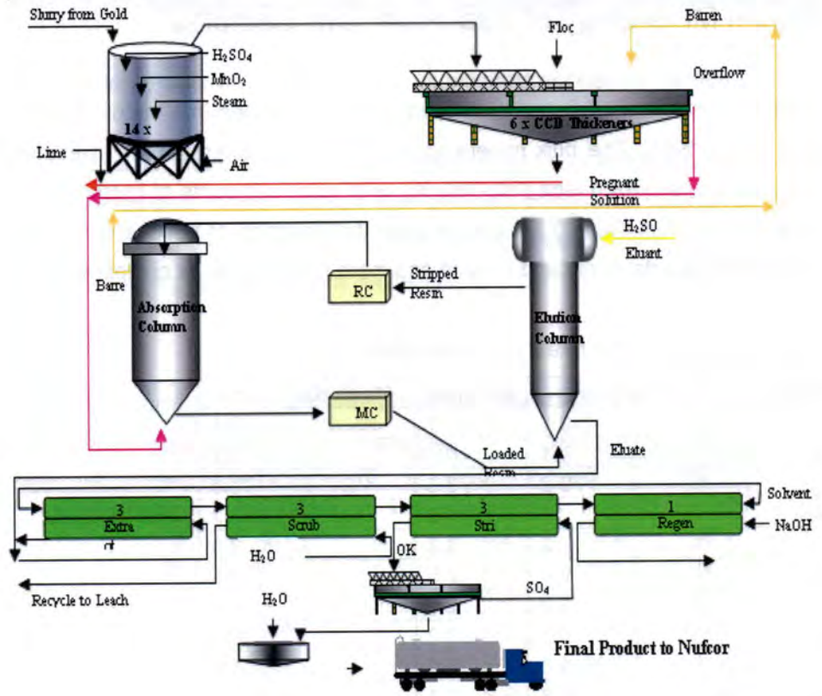

Figure 3.2: Schematic process flow diagram of the South Uranium Plant

3.3 Experimental Details

An Anglo Research sample splitting procedure (see Appendix A – Section 10.2) was used to divide the original 500 kg reef samples from the respective mines into representative portions. The samples

were first crushed to a size of ±1.7 mm before being split. Some of the samples were then further milled to 80% -75 µm and send to the geology department of Anglo Research. The samples were submitted for a mineralogical examination (to determine how the mineralogy of the three ores differ) specifically focussing on the uranium mineralogy, liberation and grain sizes. This information will be used to develop a quantitative mineralogy-reactivity relationship for acid leaching of uranium from Vaal River ores.

Samples from the three different mines were analysed on the Mineral Liberation Analyser (MLA) at Anglo Research using polished sections prepared from the sample material. The detailed uranium-mineral evaluation uses an automated sparse phase liberation measurement to identify and characterise the grains of interest in a sample block. This method detects particles with a high backscattered electron image intensity using set grey levels. The particle detected is then analysed using energy dispersive X-ray analysis and information on the particle of interest (uranium mineral) and other related phases is collected and stored. Bulk mineralogical data is obtained by using a bulk modal analysis.

3.4 Uranium Mineralogy of Vaal River Ore Samples

Like gold, uranium minerals (in the Vaal river area) are concentrated in a matrix of pebble-supported conglomerates [Smit, 1984]. The bulk mineralogies of the three different ores investigated are fairly similar and consist primarily of quartz (70 – 80 %), with lesser amounts of muscovite (8 – 11 %) as indicated in Table 3.1. From Table 3.1 it can be seen that samples of Kopanang are slightly different from, and contain less quartz, pyrite and chlorite and more pyrophyllite, as compared to the other ores.

Table 3.1: Bulk mineralogy of the three Vaal River ores

Mineral	Kopanang	Noligwa	Moab Khotsong
Uraninite	0.1	0.1	0.1
Brannerite	0.1	0.1	0.1
Quartz	70.2	73.3	79.8
Muscovite	10	11.3	8.2
Chlorite	2	3.2	3.6
Pyrophyllite	9.7	2.5	1.1
Pyrite	1.3	2.5	2.8
Carbonates	0.1	0.2	0.1
Albite	4.8	5.1	1.9
K-Feldspar	0.8	0.4	1.3
REE-phoshates	0.1	0.2	0.1
Other silicates	0.1	0.2	0.3
Other oxides	0.4	0.4	0.2
Copper	0	0	0.1
Carbon	0.2	0.5	0.3
Total	**100**	**100**	**100**

Figure 3.3 shows backscattered images of uranium minerals in carbon to illustrate the method of detecting the different minerals. The grey level is determined by the density of the mineral. A low density mineral will appear dark and a high density mineral will have a lighter colour. Finer size fractions (-10 µm and +10 µm) were also examined in more detail. If was done to determine if it is possible to consider different recovery technique (i.e floating before leaching).

Figure 3.3: Backscattered electron images of uranium minerals enclosed in carbon

From Table 3.2 it is clear that the bulk mineralogy composition of the +10 µm size fraction is very similar to the combined bulk modal analysis and primarily consists of quartz (60 % - 73 %) and muscovite (12 % - 14 %). The composition of the -10 µm size fraction differ contains lesser amount of quartz (17 % - 30 %), higher amounts of albite (17 % - 23 %), muscovite (28 % - 32 %) and pyrophyllite (12 % - 30 %).

Table 3.2: Bulk mineralogies of -10µm and +10 µm size fractions for the Vaal River ores

	Kopanang		Noligwa		Moab Khotsong	
Mineral	**-10**	**+10**	**-10**	**+10**	**-10**	**+10**
Uraninite	0	0	0	0.1	0	0
Brannerite	0.6	0.1	0.3	0.2	0.2	0.1
Quartz	16.5	60.5	26.8	66.5	29.8	72.7
Muscovite	32.1	12.7	28.5	14.3	28.3	12.2
Chlorite	1.6	2.4	4.4	4.8	3.5	3.4
Pyrophyllite	29.5	14.9	12.5	3.6	12.3	3
Pyrite	0.1	0.7	0.5	2.5	0.5	2.3
Carbonates	0	0.1	0	0.2	0	0.1
Albite	17.3	7	23.1	6	21.8	4.6
K-Feldspar	1.1	0.3	1.7	0.5	1.9	0.4
REE-phosphates	0.1	0.1	0	0	0.1	0.1
Other silicates	0.2	0.3	0.5	0.4	0.4	0.2
Otheroxides	0.3	0.6	0.4	0.3	0.3	0.4
Copper	0	0	0	0	0	0
Carbon	0.6	0.3	1.3	0.6	0.9	0.5
Total	**100**	**100**	**100**	**100**	**100**	**100**

The uranium concentrations in the different ores also varied within the following ranges: Kopanang (270 – 330 ppm), Noligwa (290 – 450 ppm) and Moab Khotsong (390 – 540 ppm). A detailed uranium mineralogical characterisation of the ore was conducted and the uranium mineral distributions are shown in Table 3.3.

Table 3.3: Uranium mineral distribution (area %) of feed samples [1]

Mineral	Formula	Kopanang (%)	Noligwa (%)	Moab Khotsong (%)
Uraninite	UO_2	47.6 (84.9)	42.1 (79.7)	52.8 (89.2)
Brannerite	$(U,Th,Ca)[Ti,Fe)_2O_6$	42.2 (12.9)	49.6 (18.5)	32.3 (7.7)
U-Phosphate	$(U, Cl)PO_4$	3.1 (0.2)	2.5 (0.1)	5.7 (0.4)
Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$	7.1 (2.0)	5.8 (1.7)	9.2 (2.7)
Total		100(100)	100(100)	100(100)

[1] Values in brackets represent uranium metal deportment (%), calculated from ideal mineral uranium contents, assuming spherical shapes to convert area to volume and then to mass of mineral using their ideal densities. There is no 'standard' U-phosphate mineral, so its uranium concentration was assumed to be the same as that of brannerite and its density that of apatite. Densities used were 10.88, 5.2, 3.19 and 5.44 g/cm^3 for uraninite, brannerite, apatite and coffinite respectively. Uranium contents used were 88.15, 33.54, and 72.63 % for uraninite, brannerite, and coffinite respectively [www.webmineral.com].

As expected from earlier studies by Smit [1984], it was found that uraninite, as well as brannerite-type minerals ($U_{1-x}Ti_{2+x}O_6$), are jointly responsible for the major portion of uranium carriers in ore from the Witwatersrand Basin. Table 3.2 shows that 80 – 90 % of the uranium in the ores is contained as uraninite, 8 – 19 % as brannerite, and the balance as traces of coffinite and uranium phosphates.

An elemental analysis per size fraction (selected key elements) were done to verify the mineral deport across the different size fractions for samples milled to ~ 80% -75 µm. The results are presented in Table 3.4, Table 3.5 and Table 3.6. Elemental analysis is expected to be more accurate for low-abundance elements than mineralogical identification.

Table 3.4: Elemental analysis of different size classes of the milled (to ~ 80% -75 µm) Kopanang ore

Element	+106µm	+75-106µm	+53-75µm	+38-53µm	+10-38µm	-10µm
Fe (%)	1.45	1.08	1.09	1.26	1.44	2.92
S (%)	0.55	0.63	0.71	0.66	0.51	0.26
Al (%)	1.94	1.80	1.63	2.1	4.4	8.48
Mg (%)	0.16	0.17	0.16	0.14	0.18	0.34
Ca (%)	0.19	0.23	0.19	0.18	0.07	0.13
Ti (%)	0.14	0.14	0.12	0.12	0.15	0.21
U (ppm)	184	278	283	266	263	244

Table 3.5: Elemental analysis of different size classes of the milled (to ~ 80% -75 µm) Noligwa ore

Element	+106µm	+75-106µm	+53-75µm	+38-53µm	+10-38µm	-10µm
Fe (%)	2.93	2.37	1.97	2.26	2.61	3.18
S (%)	1.21	1.59	1.4	1.54	1.33	0.74
Al (%)	1.52	1.73	1.52	1.81	3.18	8.39
Mg (%)	0.27	0.20	0.20	0.25	0.34	0.29
Ca (%)	0.11	0.12	0.23	0.08	0.13	0.14
Ti (%)	0.13	0.16	0.13	0.14	0.17	0.18
U (ppm)	148	220	250	265	281	277

Table 3.6: Elemental analysis of different size classes of the milled (to ~ 80% -75 µm) Moab Khotsong ore

Element	+106µm	+75-106µm	+53-75µm	+38-53µm	+10-38µm	-10µm
Fe (%)	1.73	2.25	2.05	2.15	2.72	2.59
S (%)	1.27	1.45	1.55	1.61	1.47	0.74
Al (%)	1.12	1.91	1.74	1.76	3.12	8.98
Mg (%)	0.14	0.26	0.18	0.19	0.42	0.46
Ca (%)	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.07
Ti (%)	0.08	0.15	0.13	0.12	0.17	0.13
U (ppm)	254	344	400	430	523	361

For all the samples, the +106 µm fraction has the lowest concentration of uranium. Otherwise there is no consistent uranium deportment pattern across the three ores, i.e. below 106 µm fraction the concentration of uranium is similar in all size classes. This suggests that the uranium grains are small enough to be distributed in a statistical manner across the size fractions – although nothing can be concluded regarding the uranium minerals' degree of liberation.

Uraninite dissolves readily in the presence of a lixiviant, provided that the required conditions of extraction are met. Brannerite-type minerals, unlike uraninite, are not readily leachable in sulphuric acid and therefore are referred to as refractory. Liebenberg [1955] distinguished between two uraniferous titanates in Witwatersrand ore: uraniferous leucoxene and brannerite, which have UO_2:TiO_2 mole ratios of <1 and >1, respectively. One would expect variability in the leaching response amongst brannerite-type minerals, but at this stage of the study different brannerite types were not investigated. Previous work done by Glatthaar and Duchovny [1979] indicated that Vaal River ores mostly consist of brannerite associated with leucoxene and other titaniferous minerals (termed uraniferous leucoxene) which have a more loosely knit appearance and probably are more readily available for dissolution as compared to brannerite associated with silicates (termed brannerite), which occurs as minute, compact crystals intergrown in the siliceous material. This, however, does not indicate that the different types of brannerite minerals will dissolve.

Coffinite, which is present in small amounts, is generally more reactive than brannerite to oxidative sulphuric acid leaching, but less reactive as compared to uraninite. In ore from the Elliot Lake district, which also consists mostly of brannerite and uraninite, secondary coffinite intergrowths are enhancing

the overall kinetics of brannerite by accelerating leaching pit formation [Ifill *et al.*, 1996]. Furthermore, in the ore samples investigated, there were also traces of uranium associated with monazite, which may be inert or reactive, depending on whether uranium is a substitutional impurity or is adsorptively associated with monazite. Ford and Gould [1994] found that the amount of inert uranium is, in absolute terms, fairly similar for all Witwatersrand ores, at about 0.015 kg/t to 0.030 kg/t, suggesting that there is always an amount which is very inert.

The mineralogy investigations focused on uraninite and brannerite, as they form the bulk of the uranium-bearing minerals. Table 3.7 shows the uranium-mineral associations. Most of the unliberated uraninite is associated with silicates, carbon, or has a ternary association. Moab Khotsong also has a high percentage uraninite associated with phosphates. Association with carbon is quite low for brannerite.

Table 3.7: Brannerite and uraninite associations

	Brannerite			Uraninite		
	Kopanang	**Noligwa**	**Moab Khotsong**	**Kopanang**	**Noligwa**	**Moab Khotsong**
Binary Association	**67.8**	**85.8**	**67.7**	**86.0**	**85.2**	**86.6**
Liberated	11.8	11.1	13.4	30.6	30.9	42.3
Uranium Minerals	1.7	7.5	15.7	11.8	7.1	6.5
Silicates	46.8	59.0	28.7	27.4	20.6	24.0
BMS	1.0	2.1	4.1	0.3	0.5	0.7
Oxides	3.6	4.0	4.6	0.1	0.1	0.7
REE-Phosphate	0.0	0.0	0.2	0.0	1.2	8.0
Carbonate	0.0	0.0	0.0	0.0	0.0	0.0
Carbon	2.9	2.1	1.0	15.8	24.8	4.3
Ternary Association	**32.2**	**14.2**	**32.3**	**14.0**	**14.8**	**13.4**
Total	100	100	100	100	100	100

Table 3.8: Uranium mineral grain size distribution of the samples tested of the various ores

Size Class (µm)	Kopanang	Noligwa	Moab Khotsong
106	2.8	0.9	2.5
75	7.7	6.2	6.7
53	10.0	9.1	6.5
38	7.0	19.7	16.6
27	12.8	5.7	14.7
19	4.6	17.0	4.2
13.5	18.4	5.7	15.9
9.6	8.1	12.9	7.1
5.7	11.7	9.0	6.2
4.1	16.9	13.8	9.6
Total	**100.0**	**100.0**	**100.0**
p50*(µm)	19.4	21.3	23.2

Uranium grain sizes were found to be very small, with 50 % of the particles passing 19.4, 21.3 and 23.2 µm for Kopanang, Noligwa and Moab Khotsong respectively (see Table 3.8). The degree of liberation (as defined in the next paragraph) of the uranium-bearing minerals was low (see Table 3.9 and Table 3.10), between 11 and 45 %, and expectedly increased as particle size decreased. It is important to realise that surface area exposure may be a more useful indicator of leachability of uranium minerals, as opposed to intrinsic liberation. Minerals with exposed surface area are technically leachable as they can be accessed by a lixiviant. Table 3.9 and Table 3.10 also show that between 87 and 93 % of the uraninite particles and 71 to 86 % of the brannerite particles have more than 10 % of their surfaces exposed, and even higher proportions have more than 5 % of their surfaces exposed.

Table 3.9: Percentage uraninite liberation and percentage of uraninite with 5 and 10 % surface exposure

	Kopanang (%)	Noligwa (%)	Moab Khotsong (%)
Liberated	30.6	30.9	42.3
Middlings	26.1	31.6	31.2
Locked	43.3	37.5	26.5
Total	**100**	**100**	**100**
5 % Surface Exposure	96.4	96.4	98.3
10 % Surface Exposure	88.9	87.4	93.2

Table 3.10: Percentage brannerite liberation and percentage of brannerite with 5 and 10 % surface exposure

	Kopanang (%)	Noligwa (%)	Moab Khotsong (%)
Liberated	11.8	11.1	13.4
Middlings	38.7	53.4	29.6
Locked	49.5	35.5	57.0
Total	**100**	**100**	**100**
5 % Surface Exposure	93.9	94.2	87.8
10 % Surface Exposure	79.3	86.1	71.3

Figure 3.4 shows the distinction between liberation and surface exposure. It is suggested that the measurement of area exposure of the uranium minerals (especially the fraction with > 10 % of surface exposed) is a very good indicator of their leachability, because only intrinsic inertness to leaching reagents can cause an exposed mineral to remain unleached.

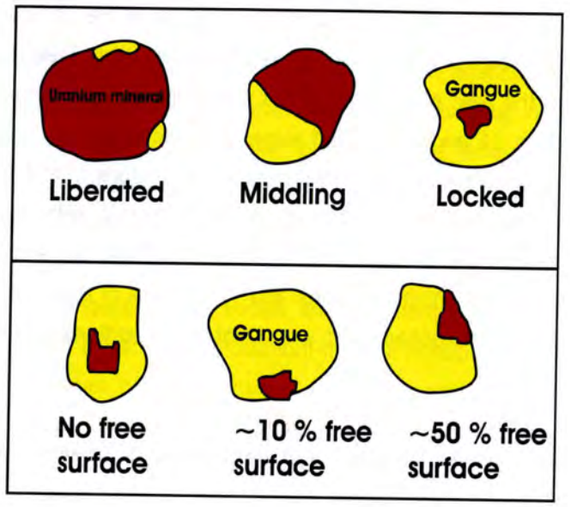

Figure 3.4: Distinction between liberation and surface exposure

3.5 Summary

Bulk mineralogy showed that the uranium samples investigated consist predominantly of quartz with lesser amounts of muscovite. The Kopanang samples are slightly different containing more pyrophyllite and lesser pyrite and chlorite. The mineralogical study of the different ores also confirms that the main uranium carriers in the Vaal River ores are uraninite and brannerite. Uranium minerals seem to have a high percentage surface area exposure, despite poor liberation. This suggests that the breakage of the ore particles occurs near the uranium grains, and it therefore needs to be established whether this is due to association with soft gangue components. This means that coarser grinds can be tolerated for uranium leaching than one would suspect from their grain sizes alone. Moreover, based on this information, it is safe to assume that the uranium minerals will be exposed to the leaching environment.

Chapter 4

Standard Uranium Acid Leaching

Today, as the uranium price is rising, there is scope for finding opportunities to increasing uranium recovery form less conventional resources, as well as to reduce operating costs. The most expensive and critical unit operation in uranium extraction is the leaching step. The interrelationship between mineralogy, mineral liberation and the leaching behaviour of uranium is still not well defined. A better understanding of these relationships, could give insight as to what extent the differences in percentage uranium recovery (from different mines) represent differences in ore characteristics, or differences in leaching practice.

This chapter focuses on standard laboratory leaching tests to determine the effect of both leaching conditions and mineralogical features of the ore on the ultimate extraction of uranium within the parameter space that is attainable in plant operation. The leaching behaviour of ores from three mines in the Vaal River Region; Kopanang, Noligwa and Moab Khotsong were examined.

4.1 Experimental Details

4.1.1 Sample Preparation

The Anglo Research sample splitting procedure was used to divide the original 500 kg reef samples from the mines (Kopanang, Great Noligwa, and Moab Khotsong) into representative portions. The samples were first crushed to a size of ±1.7 mm before being split.

To avoid erroneous results due to pre-oxidation of the ore whilst in storage, the ore samples required for a specific test were milled to the target P_{80} size and dried a day before carrying out the actual experiments. Unless stated otherwise, the ore samples were rod-milled to a P_{80} of -75µm (see Appendix B – section 11.4 for the PSD graph).

4.1.2 Testing Procedure and Conditions

4.1.2.1 Standard Leaching Tests

Factorial design setup (2^3 design) was proposed for testing the dependence of the percentage uranium extraction on individual parameters, and to investigate interactions between the variables for simultaneous variations of parameters.

Key parameters investigated in the uranium leaching experiments, and their ranges, were:

- Sulphuric acid addition (9.9 kg/t , 12.8 kg/t , 16.3 kg/t)
- Temperature (40°C, 50°C, 60°C)
- MnO_2 addition (2 kg/t, 3 kg/t, 4 kg/t – as 100 percent MnO_2)

The leaching experiments were carried out in 2L water-jacketed batch reactors, which were mechanically agitated. Sulphuric acid was added as a 647 g/L H_2SO_4 solution. Pyrolusite containing 29.3 % MnO_2 and 36.5 % Fe was used as a solid oxidant. The absolute dosages were calculated on the basis of a pulp RD of 1.55 and a solids SG of 2.7. Stirring speed was kept constant at 6 rpm. A photo of the experimental setup is presented in Figure 4.1 and the standard working procedure, list of apparatus, chemicals and PPE required are included in Appendix B – Section 11.1. The concern in using a two level factorial design is the assumption of linearity. Consequently, 3 centre points (Temp: 50°C, Acid: 12.8 kg/t, MnO_2: 3 kg/t) were included to test for quadratic curvature and to allow independent estimation of the error.

Figure 4.1: Photo of the experimental setup for the standard leaching tests

The pulp mixture consisting of 1310 g ore and 1015 ml water was pre-heated for 1 hr to the test temperature, before the start of each experiment. Sulphuric acid was added to the mixture at time t=0, signifying the start of the experiment. After 1.5 hours, the solid oxidant (pyrolusite) was added. Absolute dosages are presented in Table 4.1. Uranium dissolution and reagent consumptions were monitored over a 24 hr leach period. Slurry samples of 170 ml were collected and filtered at sampling times 1, 3, 4.5, 6, 10 and 24 hrs. pH and Eh of the filtered solution samples were measured at room temperature. The solutions were analysed for [U^{6+}], [Fe], [Fe^{2+}], [Mn^{2+}] and [H^+], while solids were analysed for U and Fe only. For each test, a head sample (40 g) was analysed for U and Fe.

Table 4.1 Absolute reagent dosages in the standard tests

Reagent	Dosage
H_2SO_4 - 9.9 $^{kg}/_t$	20 ml
H_2SO_4 – 12.8 $^{kg}/_t$	26 ml
H_2SO_4 – 16.3 $^{kg}/_t$	33 ml
H_2SO_4 – 25 $^{kg}/_t$	51 ml
MnO_2 - 2 $^{kg}/_t$	8 g pyrolusite
MnO_2 - 3 $^{kg}/_t$	12 g pyrolusite
MnO_2 - 4 $^{kg}/_t$	16 g pyrolusite

In the discussions that follows there will be reference to mild, mid, aggressive and most aggressive conditions, which are defined as follows: **Mild**: Temperature: 40°C, H_2SO_4: 9.9 kg/t, MnO_2: 2 kg/t, **Mid**: Temperature: 50°C, H_2SO_4: 12.8 kg/t, MnO_2: 3 kg/t, **Aggressive**: Temperature: 60°C, H_2SO_4: 16.3 kg/t, MnO_2: 4 kg/t, **Most aggressive**: Temperature: 60°C, H_2SO_4: 25 kg/t and MnO_2:4 kg/t.

4.1.2.2 Additional Tests

As more conceptual questions arose, additional experiments were planned and executed. The experiments, and the reasons why they were conducted, are described in Table 4.2.

Table 4.2: Additional tests that were conducted

Test description	Conditions	Motivation
Most aggressive leaching	Acid addition increased to 25 $^{kg}/_{t}$ while keeping temperature and MnO_2 at 60°C and 4 $^{kg}/_{t}$ respectively.	To see if overdosing with acid will increase uranium recovery.
Coarse grind	Tests at coarser grinds of 40 % -75 µm and 60 % -75µm.	To establish sensitivity of uranium extraction to the degree of comminution, at the lower end, as comminution is expensive.
Low density	Halve the quantity of ore in the reactor while keeping the volume of water at 1015 ml.	To test if there is a limitation on uranium extraction due to uranium solubility approaching its maximum.
Leaching using HNO_3	Use nitric acid instead of sulphuric acid and solid oxidant. Base dosage on adding moles comparable with a selected sulphuric acid test.	To determine if leaching at higher potentials (expected for HNO_3) will lead to uranium extractions approaching 100 %.
Constant pH	Keep the pH at a value ≤1 using an autotitrator.	To see if a constant low pH can improve dissolution of uranium.
Extended leaching tests	Leaching for 48 hours.	To determine if the 24 hr leaching time limits achievable uranium dissolutions.

4.2 Results and Discussion

4.2.1 General Trends in Uranium Dissolution

Uranium dissolutions (%) after a 24 hour leaching period are presented in Table 4.3 – 4.5. Note that percentage dissolution is based on solid analyses, as this was seen to be a more reliable measure of dissolution (see Appendix B –section 11.5 for indicative mass balances). The independent estimate of error (based on centre-point triplicates) determined for Kopanang, Noligwa and Moab Khotsong for 24 hours were 1.5, 0.4 and 2 percentage points, respectively.

Table 4.3: Percentage uranium dissolution after 24 hrs for Kopanang ore. Acid consumption is included in kg/t in brackets.

	High Temp(60°C)	High Temp(60°C)	Low Temp(40°C)	Low Temp(40°C)
High Acid(16.3kg/t)	90.3 (11.2)	86.6 (13.3)	85.2 (12.8)	87.4 (10.8)
Low Acid(9.9kg/t)	63.8 (9.2)	68.3 (8.3)	63.8 (8.7)	68.0 (8.0)
	High MnO_2(4kg/t)	Low MnO_2(2kg/t)	High MnO_2(4kg/t)	Low MnO_2(2kg/t)

Table 4.4: Percentage uranium dissolution after 24 hrs for Noligwa ore. Acid consumption is included in kg/t in brackets.

	High Temp(60°C)	High Temp(60°C)	Low Temp(40°C)	Low Temp(40°C)
High Acid(16.3kg/t)	83.5 (14.8)	86.2 (14.2)	86.7 (11.9)	83.1 (11.6)
Low Acid(9.9kg/t)	71.8 (9.6)	73.7 (9.2)	76.5 (9.0)	69.8 (8.6)
	High MnO_2(4kg/t)	Low MnO_2(2kg/t)	High MnO_2(4kg/t)	Low MnO_2(2kg/t)

Table 4.5: Percentage uranium dissolution after 24 hrs for Moab Khotsong ore. Acid consumption is included in kg/t in brackets.

	High Temp(60°C)	High Temp(60°C)	Low Temp(40°C)	Low Temp(40°C)
High Acid(16.3kg/t)	80.5 (15.9)	66.7 (15.4)	80.0 (13.7)	79.8 (12.6)
Low Acid(9.9kg/t)	67.9 (9.6)	70.9 (9.4)	70.3 (9.3)	70.9 (8.9)
	High MnO_2(4kg/t)	Low MnO_2(2kg/t)	High MnO_2(4kg/t)	Low MnO_2(2kg/t)

Over the parameter space considered in the standard tests, the factor that has the greatest influence on uranium dissolution appears to be the acid addition. Uranium dissolution improves from ~ 70 % at an acid addition of 9.9 kg/t to ~ 80 % at an addition of 16.3 kg/t for Moab Khotsong and Great Noligwa ores. Linearly simplified, this amounts to an improvement of ~ 1.5 percentage points per kg/t increase in acid addition over the range considered. Kopanang ore behaves qualitatively similarly but quantitatively slightly different, in that the low-end dissolution is lower (~ 65 %) and the high-end dissolution is higher.

The insensitivity of the dissolution to temperature changes is indicative of a mass-transfer (could be internal or external) controlled reaction. With regards to the solid oxidant effect, interactions between variables cannot be ignored. For example, a low oxidant addition/high temperature combination can give the same result as a high oxidant/low temperature combination, in accordance with Nernst equation:

$$\Delta E = \Delta E^{o} - \frac{RT}{nF}\ln\frac{Fe^{2+}}{Fe^{3+}} \qquad [4.1]$$

In a Butler-Volmer formalism, the overpotential affects the reaction rate exponentially. Therefore the influence of the absolute Fe^{3+}/Fe^{2+} ratio (controlled by solid oxidant addition and reactivity of Fe-bearing ore constituents) on the rate will actually only be linear.

A statistical description of the data in Table 4.3 – 4.5 was carried out using the computer package Design Expert 6®. The software basically gives empirical formulae, describing the percentage dissolution for the various ores. The empirical formulae obtained were (Units of variables: **T**emperature (°C), **A**cid (kg/t), **O**xidant (kg/t)):

Kopanang Uranium Dissolution (%)

*= 22.51875 + 0.56914*T + 4.93750*A + 5.98906*O - 0.055469*T*A – 0.24090*T*O – 0.79687*A*O + 0.023828*T*A*O* [4.2]

Noligwa Uranium Dissolution (%)

*= 3.14063 +0.86477*T + 3.53125*A +17.90547*O – 0.024219*T*A – 0.30395*T*O – 0.60156*A*O + 0.00898477*T*A*O* [4.3]

Moab Khotsong Uranium Dissolution (%)

*= -35.85781 + 2.37070*T + 10.35937*A + 26.23125*O – 0.22734*T*A – 0.67875*T*O – 2.43750*A*O + 0.0625*T*A*O* [4.4]

Equations [4.2] to [4.4] have limited explanatory value, and should only be considered as a 'packaging' of experimental data inside the operating window considered in this work.

Table 4.6: Comparison of uranium dissolutions and acid consumptions between aggressive (Acid: 16.3kg/t) and most aggressive (Acid: 25kg/t) conditions at 60°C and MnO_2 addition of 4 kg/t[1].

Ore Type	Uranium Dissolution at Aggressive Conditions (%)		Uranium Dissolution at Most Aggressive Conditions (%)	
	Experimental Value	Statistical Model Prediction	Experimental Value	Statistical Model Prediction
Kopanang	90.3 ($11.2^{kg}/_{t}$)	90.3	89.0 ($18.6^{kg}/_{t}$)	100
Great Noligwa	83.5 ($13.9^{kg}/_{t}$)	83.5	85.5 ($22.2^{kg}/_{t}$)	99.4
Moab Khotsong	80.5 ($15.9^{kg}/_{t}$)	80.5	84.0 ($22.5^{kg}/_{t}$)	97.6

[1]Note that acid consumptions are given in parenthesis alongside uranium dissolutions in Table 4.6. Predicted dissolutions based on the statistical correlations are also given, to illustrate the limitations of statistically-derived empirical formulae.

Evaluating the standard test results it became clear that acid addition has the greatest influence on uranium dissolution. This motivated the experiment at a higher acid addition of 25 kg/t, at the aggressive temperature and solid oxidant levels. The results are shown in Table 4.6. Predictions

based on the empirical formulate (equations [4.2] to [4.4]) are also shown, for interest's sake. Values in brackets represent acid consumption of the ore (difference between acid added and free acid after 24 hrs). Clearly, the dissolutions appear to have reached a maximum, either due to mineralogical, liberation or mass transport limitations. The poor predictive power of the statistical correlations is clear from the data (they predict complete dissolution at elevated acid levels).

4.2.2 Effect of Oxidising Power of the Solution

Uranium dissolution over the parameter space never exceeded 90 %, even under maximum attainable plant conditions. One wonders whether at any stage during the reaction, there is an insufficient absolute amount of Fe^{3+} to act as electron acceptor for the UO_2 that is left in the ore. According to reaction [1.1], an Fe^{3+}:UO_2 molar ratio of 2 is required for each redox cycle. Figure 4.2 shows the Fe^{3+}:UO_2 molar ratio for the three ores under aggressive conditions for each sample over the 24 hr period.

It can be seen that towards the end of the reaction the uranium in the solid is not at all starved of Fe^{3+}, i.e. the absolute amount of Fe^{3+} in solution is more than enough to satisfy the stoichiometric requirements of all the uranium in the solids. The question that follows is then whether the Fe^{3+}/Fe^{2+} ratio itself is sufficient enough to result in the required redox potential for UO_2^{2+} (free or complexed) to exist as a stable solution complex, in addition to the kinetic effect of the overpotential.

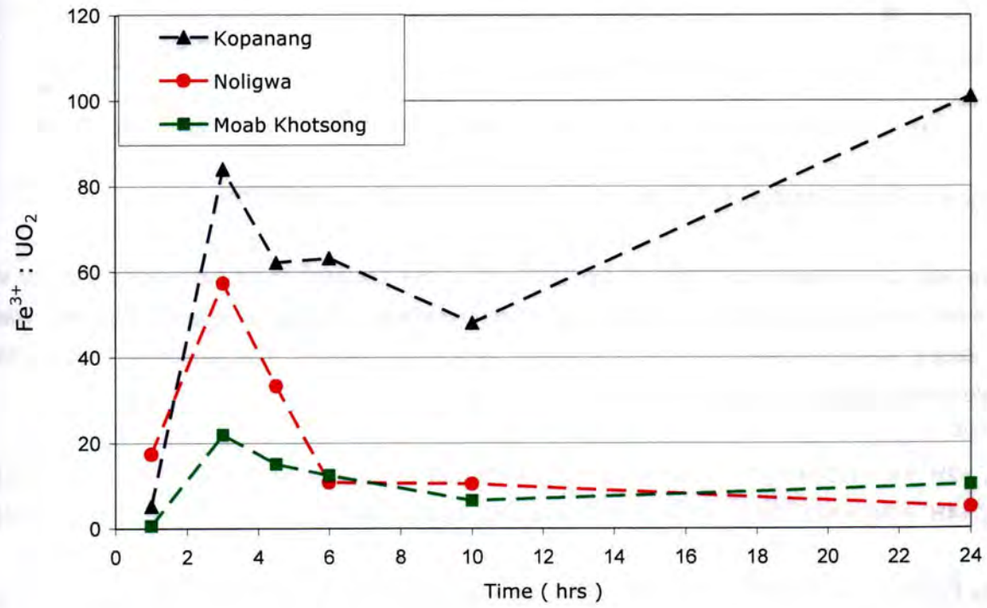

Figure 4.2: Fe^{3+}:UO_2 molar ratio over the 24 hour period (aggressive leaching conditions)

Potentials greater than 400 mV (vs SCE) are generally necessary for leaching to occur. Figure 4.3, which shows the potential as a function of time for the three ores under aggressive conditions, shows that the required potential is generally provided throughout the course of the leaching experiments. Note that the steep increase in potential at the 3 hr sample is due to the addition of solid oxidant, MnO_2, after 1.5 hours. A high potential was already measured after 1 hr reaction time (before adding pyrolusite). This is due to the leaching of Fe from the ore and was observed for all experiments and for all ores (see Appendix B – Section 11.7). It is proposed that the higher redox potential observed for Kopanang ore, post addition of pyrolusite, is due to the lower quantity of Fe leached from this ore (i.e. an added absolute amount of solid oxidant will have a higher effect on Fe^{3+}/Fe^{2+} ratio when the total Fe in solution is lower).

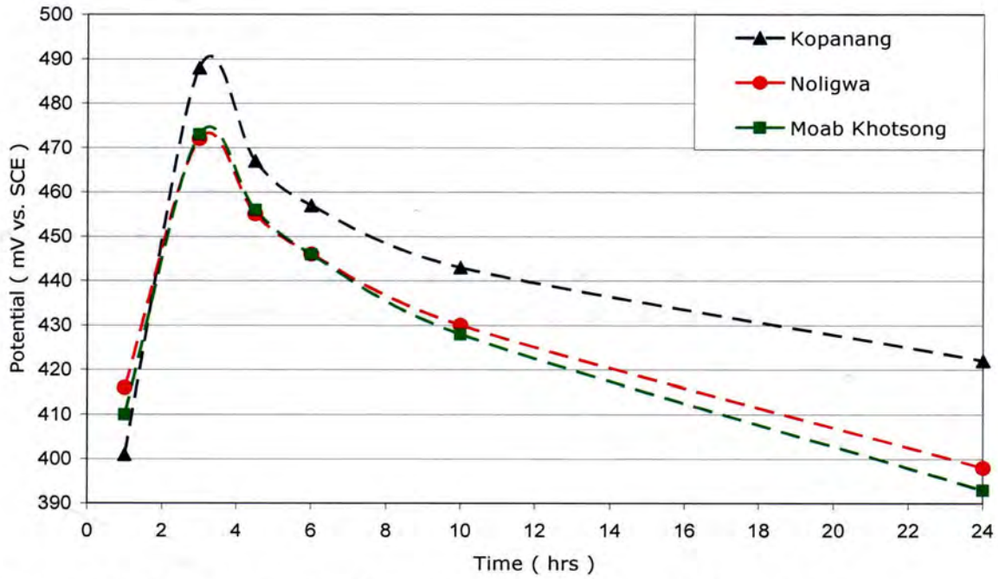

Figure 4.3: Redox potential vs. time for the 3 ores (aggressive leaching conditions)

There was still curiosity over whether the tailing-off of the potential could have been a factor in achieving top-end dissolutions of only 90 %. Therefore, test work at a higher potential than pyrolusite can supply was considered. Nitric acid is known as a strong oxidant. The reduction reactions for nitrate ions in acidic solutions are:

$$NO_3^- + 2H^+ + e^- = NO_2 + H_2O \quad (E^0 = +800 \text{ mV vs SHE, } 530 \text{ mV vs } Hg_2Cl_2) \qquad [4.5]$$

$$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O \quad (E^0 = +960 \text{ mV vs SHE, } 690 \text{ mV vs } Hg_2Cl_2) \qquad [4.6]$$

E^0 for Fe^{3+}/Fe^{2+} equals 770 mV vs. SHE, or 500 vs. Hg_2Cl_2. Nitric acid tests were performed by adding 0.44 moles of HNO_3 per litre of solution, which is between the molar amount of H_2SO_4 and H^+ added in the aggressive leach conditions. No pyrolusite was added in the nitric acid tests, and the temperature was set to 60°C. The results are shown in Figure 4.4 – Figure 4.6. As expected, the redox potential in

the nitrate tests is higher than the potential for the conventional tests. However, dissolution of uranium is not improved beyond 90 %.

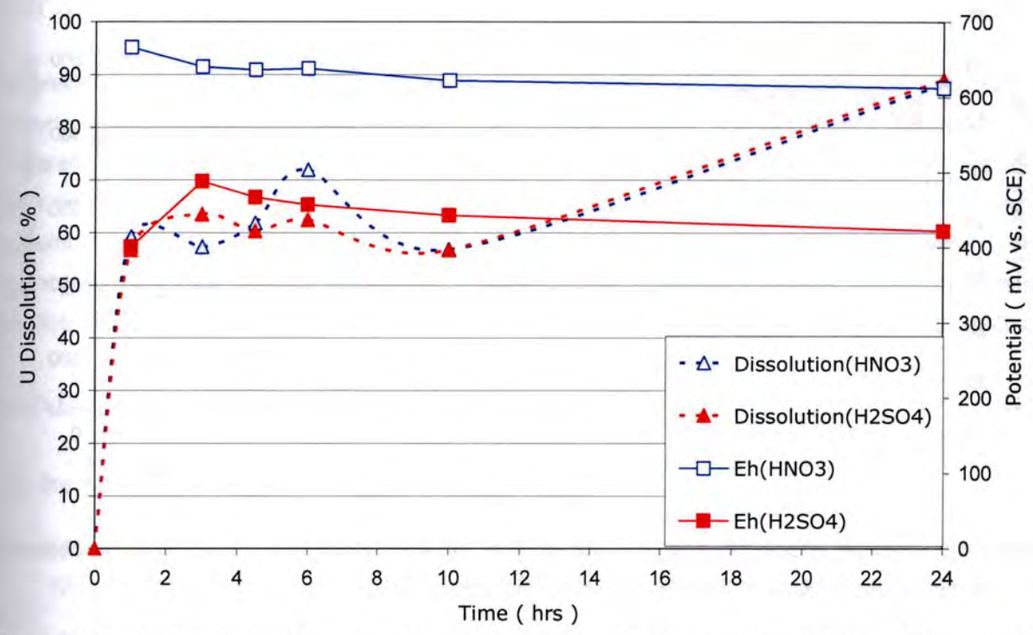

Figure 4.4: Uranium dissolution and potential vs. time for Kopanang ore: comparison between nitric and sulphuric acids at the most aggressive leaching conditions

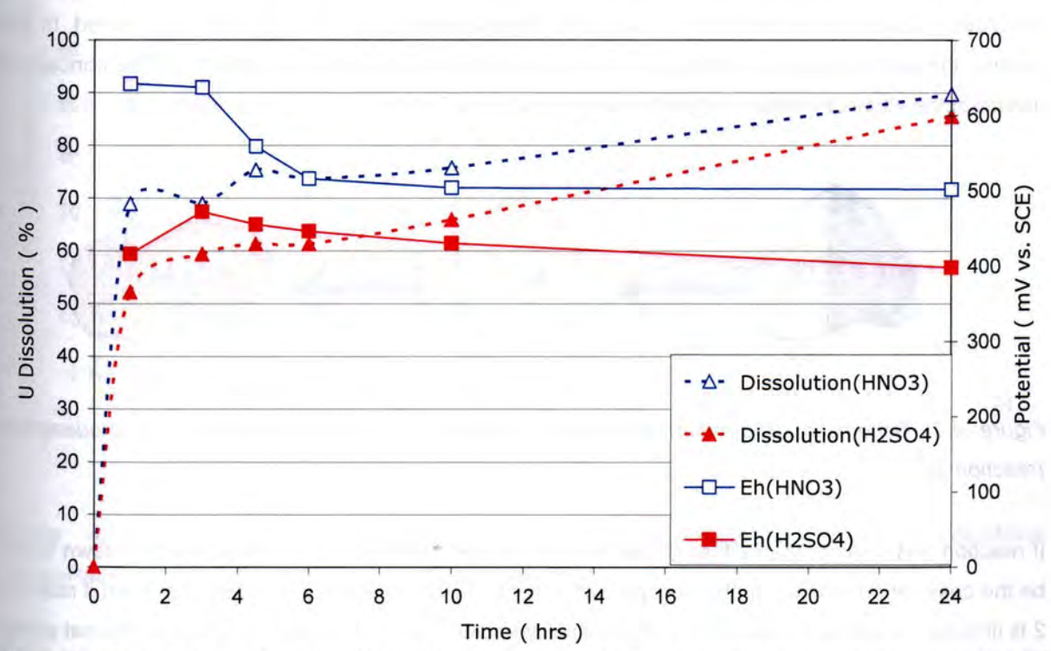

Figure 4.5: Uranium dissolution and potential vs. time for Noligwa ore: comparison between nitric and sulphuric acids at the most aggressive leaching conditions

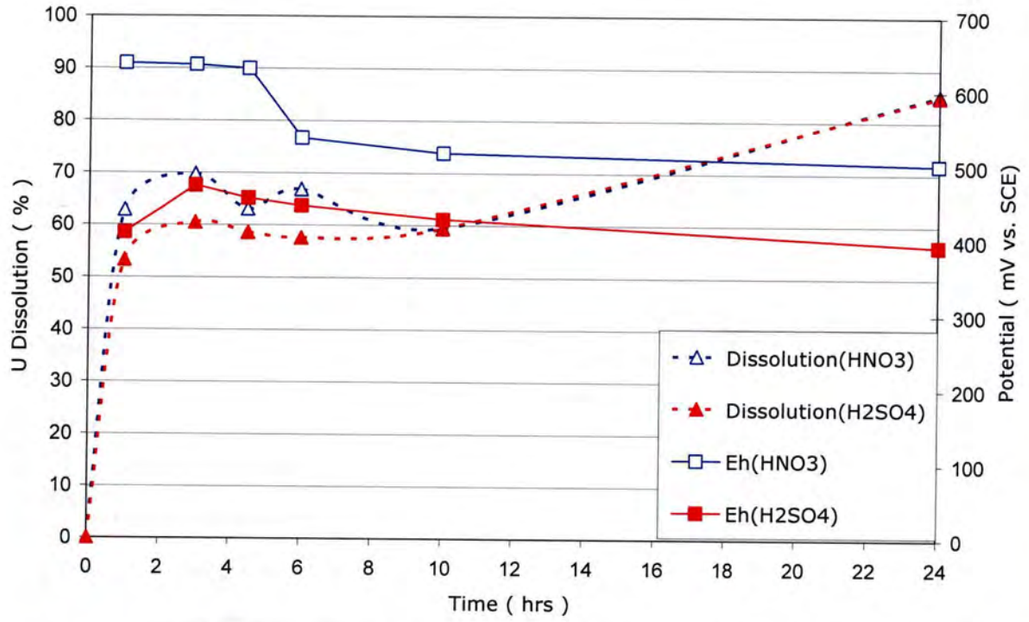

Figure 4.6: Uranium dissolution and potential vs. time for Moab Khotsong ore: comparison between nitric and sulphuric acids at the most aggressive leaching conditions

4.2.3 Possibility of Uranium Solubility Limitations

From the results presented so far it appears that reagent dosage limitations are not limiting further dissolution of uranium beyond 90 %. Therefore, physical limitations must also be investigated. In this section, the possibility of a limitation due to the solubility limit of uranium is discussed. The conceptual picture of the situation considered is illustrated in Figure 4.7.

Figure 4.7: Schematic of uranium dissolution (reaction 1) and re-precipitation or re-adsorption (reaction 2)

If reaction 1 is limiting, then either (i) the oxidising power of the solution is not enough (shown to not be the case) or (ii) uranium in the host particle is not sufficiently exposed. On the other hand if reaction 2 is limiting it is possible that either (i) the solubility of UO_2^{2+} is near its limit, such that additional uranyl ions formed re-precipitate, or (ii) some of the gangue components act as re-adsorption sites for uranyl ions.

The solubility of UO_2^{2+} decreases with increasing pH, and above a pH of 2.0, UO_2^{2+} precipitates according to the reaction [Eligwe *et al.*,1982]

$$UO_2^{2+} + 3H_2O = UO_2(OH)_2H_2O + 2H^+ \quad [4.7]$$

In previous work done on leaching of Kopanang ore, Phala [2005] found that it was necessary to include a limiting re-precipitation reaction in order to model the dissolution-time behaviour. The mineralogical characteristics of the ore were not sufficiently included in the model. In their vacation work project at AngloGold Ashanti's South Uranium Plant, Bonthuys and Mhlungu [2005] found that a maximum concentration of uranium in solution existed. Having observed that leaching seems to stop quite early on in the leaching section but resumes in the subsequent counter current decantation section following introduction of uranium-lean solution, they proposed the following empirical equation:

$$[U_3O_8]_{max}^{solution}\,(g/L) = 0.478 + 0.0298[H_2SO_4](g/L) - 0.0049T(^oC) \quad [4.8]$$

(for the temperature range 40-60°C and free acid range 3-8g/L)

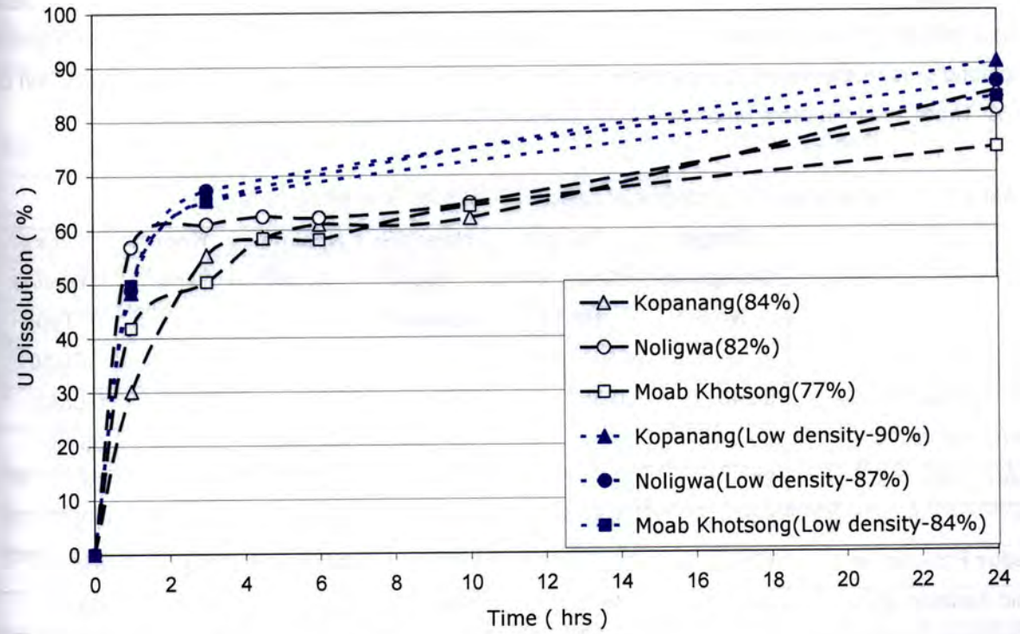

Figure 4.8: Dissolution-time behaviour at different pulp densities. Reaction conditions: Temperature : 50°C, Initial H_2SO_4 : 0.17 M, Initial MnO_2 : 3.8 g/L

If this interpretation is correct, then leaching at lower densities should result in higher dissolutions for the same solution conditions as the high density experiments. By halving the quantity of ore in the

reactor, a low pulp density of 1.33 g/cm^3 resulted. The comparison is shown in Figure 4.8. For the conditions used, the low density dissolutions were slightly higher than the dissolutions at the base case density. However, the differences were not as drastic as one would have expected. It is also possible that the rate increase is due to a higher absolute reagent: ore ratio, and not necessarily due to an increase in solubility. Therefore, these results do not support or disprove the solubility theory.

The solubility theory is further put in doubt by the fact that Australian and Canadian ores typically have much higher uranium concentrations, but high dissolutions are achieved at the same reaction conditions as the ones employed here. An example is given in Table 4.7.

Figure 4.9 shows the intrinsic solubility of uranium oxides as a function of pH. Clearly, there should not be any solubility limitations below a pH value of, say 2. A question that remains is whether leaching at conditions where solubility is very high (i.e. a pH value below 1) would result in improvements in dissolution. The results of the experiments where the pH was kept below 1, using an autotitrator, are shown in Table 4.8. Note that highly acidic conditions, like highly oxidising conditions, could also help in the destruction of the host minerals that may be locking up uranium-bearing minerals. Maintaining a constant high acidity will promote gangue reactions and result in much higher acid consumptions. It will practically be an optimisation exercise between unlocking of uranium values and accelerated acid consumptions. The results show that the dissolution is really capped at ~ 90 % for Noligwa and Moab Khotsong ores. A significant improvement is observed for Kopanang ore, with a terminal dissolution of 93 %. There must therefore be a mineralogical limit to further uranium dissolution.

Table 4.7: Optimum leaching conditions of selected Australian ores [Ring,1979]

	Ranger Composite No.5[1]	Ranger Composite No.13[1]	Nabarlek High Grade[1]	Nabarlek ROM[1]	Koon-Garra[1]	Roxy Downs Type RD10[2]
Head grade,% U_3O_8	0.248	0.359	7.79	1.61	0.451	0.0548
Temperature, °C	35	35	35	40	35	55
Leach Time, hrs	24	24	20	20	16	24
pH	1.8	1.8	1.25	1.6	1.9	1.5
Redox Potential, mV	475	475	475	480	475	650
Acid Addition, kg/t	37	48.7	105	55	41.5	50.4
Pyrolusite Addition, kg/t	4	6.398	19	7	5.9	8.3
Uranium Extraction, %	88.2	90.2	98	96.7	93.2	86.9

[1]Slurry density = 55 wt% solids and particle size = 50% -74µm
[2]Slurry density = 50 wt% solids and particle size = 80% -74µm

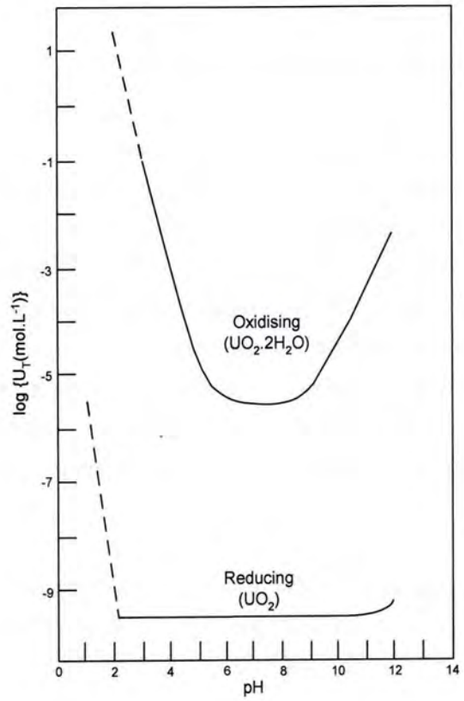

Figure 4.9: Solubility of uranium dioxide(UO_2) and schoepite($UO_3.2H_2O$) as a function of pH at 25°C [Santos et al., 2005]

Table 4.8: Results of constant pH (pH = 1) tests (T= 50°C and MnO_2 addition = 3 kg/t)

Ore Type	Uranium dissolution (%)
Kopanang	93.3
Great Noligwa	90.5
Moab Khotsong	90.7

4.2.4 Mineralogical Limitations

Having considered several possible explanations for the terminal dissolutions of ~ 90 %, with no truly firm success, the next step was to consider a mineralogical limitation. The starting point is the uranium mineralogy of the three ores, shown in Table 3.3.

As discussed in Chapter 3, the major uranium bearing minerals in these ores are uraninite and brannerite. Uraninite dissolves readily, while brannerite is generally considered to be unreactive. Uranium phosphates are either inert or reactive depending on whether uranium is a substitutional impurity or adsorptively associated with phosphate. Coffinite is generally more reactive than brannerite, but less reactive than uraninite. Liberated uranium grains were found to be very small, with 50 percent of the particles passing 19.4, 21.3 and 23.2 µm for Kopanang, Noligwa and Moab Khotsong, respectively.

Liberation of the uranium minerals was found to be quite poor (see Chapter 3) but it does not necessary imply poor uranium recovery. As discussed in Chapter 3, the mineralogy study showed high surface exposure despite poor liberation, indicating that coarser grinding can be tolerated than what would be expected. For very high liberation and surface area exposure can lead to the same conclusions regarding the leachability of a given mineral, but opposite conclusions can not necessary be reached when liberation is very poor and high surface area exposure. The assumption that surface exposure is a good explanation for high dissolutions at low liberations, and also a factor that determines maximum dissolution, need to be evaluated using mineralogical analysis of the residue samples. Attempts to 'worsen' liberation by milling coarser did not result in a decrease in dissolution (see Table 4.9). It is only possible to explain these unusual results by assuming that surface area exposure determines the leachability of the ore and therefore is a better indication for expected uranium recovery compared to actual liberation, but examining the residue samples put doubt to this statement.

Table 4.9: Uranium dissolution (%) as a function of grind (medium conditions).

	40 % -75µm	60 % -75µm	80 % -75µm
Kopanang	85	81	84
Great Noligwa	82	79	82
Moab Khotsong	71	73	77

Mineralogical analysis of the residue presented in Table 4.10 and Table 4.11 suggested that most of the uranium in the residue exists as brannerite. With regards to uraninite, it seemed to have been mostly dissolved – only small amounts remained in the residue. Therefore, surface area exposure of uraninite maybe a good indication to expected uraninite leaching but it seems not to be true for brannerite leaching.

Table 4.10: Uranium mineralogy(expressed as %) for the residue samples of mid conditions as well as aggressive conditions (24 and 48 hours) for Kopanang, Noligwa and Moab Khotsong ore

Mineral	Kopanang 24h Mid Cond	Noligwa 24h Mid Cond	Moab Khotsong 24h Mid Cond	Kopanang 24h Aggressive Cond	Kopanang 48h Aggressive Cond	Noligwa 24h Aggressive Cond	Noligwa 48h Aggressive Cond	Moab Khotsong 24h Aggressive Cond	Moab Khotsong 48h Aggressive Cond
Uraninite	9.4	14.8	3.3	9.5	33.4	1.0	6.5	10.2	1.8
Brannerite	71.4	80.3	88.4	69.9	54.4	91.2	82.8	73.6	92.7
U-Phosphate	18.1	4.8	3.6	15.8	8.1	7.3	6.5	10.4	4.0
Uth-silicate	1.1	0.1	4.7	4.8	4.1	0.5	4.2	5.8	1.5
Total	100	100	100	100	100	100	100	100	100

Table 4.11: Uranium mineralogy (expressed as %) for the residue samples of 40% -75 µm as well as 24h and 48h nitric leaching for Kopanang, Noligwa and Moab Khotsong ore

Mineral	Kopanang 40% -75 µm 24h Mid Conditions	Noligwa 40% -75 µm 24h Mid Conditions	Moab Khotsong 40% -75 µm 24h Mid Conditions	Kopanang 24h HNO_3 Leach	Kopanang 48h HNO_3 Leach	Noligwa 24h HNO_3 Leach	Noligwa 48h HNO_3 Leach	Moab Khotsong 24h HNO_3 Leach	Moab Khotsong 48h HNO_3 Leach
Uraninite	5.2	6.5	14.8	8.0	3.9	1.0	0.5	0.6	0.9
Brannerite	91.6	84.8	76.9	74.5	90.0	84.7	92.3	96.0	83.4
U-Phosphate	2.6	7.5	6.3	16.3	3.8	9.2	3.4	2.1	10.1
Uth-silicate	0.6	1.2	2.0	1.2	2.3	5.1	3.8	1.3	5.6
Total	100	100	100	100	100	100	100	100	100

Investigating the liberation and surface area exposure of the residue brannerite, it seems that brannerite is exposed to the lixiviant (Table 4.12 and Table 4.13). Therefore, neither liberation nor surface area exposure is expected to influence optimum uranium recovery. This leads to the question is brannerite intrinsically inert or not.

Table 4.12: Percentage brannerite liberation and percentage of brannerite with 5 and 10 % surface exposure for residue samples of mid conditions as well as aggressive conditions (24 and 48 hours) for Kopanang, Noligwa and Moab Khotsong ore

Brannerite	Kopanang 24h Mid Conditions	Noligwa 24h Mid Conditions	Moab Khotsong 24h Mid Conditions	Kopanang 24h Aggressive Conditions	Kopanang 48h Aggressive Conditions	Noligwa 24h Aggressive Conditions	Noligwa 48h Aggressive Conditions	Moab Khotsong 24h Aggressive Conditions	Moab Khotsong 48h Aggressive Conditions
Liberated	37.5	25.6	16	26.5	5.7	12	53	41	64.9
Free surface >5%	92.2	86.7	89	88.9	58	92	90	90	81.3
Free surface >10%	91.6	74.6	80	86.2	58	85	84	86	75.9

Table 4.13: Percentage brannerite liberation and percentage of brannerite with 5 and 10 % surface exposure for the residue samples of 40% -75 µm as well as 24h and 48h nitric leaching for Kopanang, Noligwa and Moab Khotsong ore

Brannerite	Kopanang *40% -75 µm* 24h Mid Conditions	Noligwa *40% -75 µm* 24h Mid Conditions	Moab Khotsong *40% -75 µm* 24h Mid Conditions	Kopanang 24h HNO_3 Leach	Kopanang 48h HNO_3 Leach	Noligwa 24h HNO_3 Leach	Noligwa 48h HNO_3 Leach	Moab Khotsong 24h HNO_3 Leach	Moab Khotsong 48h HNO_3 Leach
Liberated	17.3	31.4	11.6	59.5	19.0	26.0	27.8	33.1	27.4
Free surface >5%	87.8	79.7	74.3	82.1	94.5	81.6	85.9	84.3	76.9
Free surface >10%	87.1	71.6	71.4	72.7	92.3	72.7	79.2	83.3	66.3

The high brannerite content in the ore, however, suggests that some of it has been dissolved in the course of achieving ~ 90 % total uranium dissolution (see Table 3.3). From the free energies of formation of UO_2 and UO_2^{2+} [Ulmann's Encyclopaedia, 1996; U.S.N.B.S. Tables, 1982], it was calculated that a potential of 0.39 V (vs. SHE) is required to oxidise pure uraninite to UO_2^{2+}. Zhang *et al.* [2003] studied synthetic brannerite samples and found that under acidic environments, uranium release from brannerite is incongruent, meaning that UO_2 is released while TiO_2 is left behind. The enthalpy for the reaction of synthetic brannerite (UTi_2O_6) to UO_2 and TiO_2 is 7.7±2.8 kJ/mol [Helean *et al.*, 2003]. If the free energy is assumed to be approximately equal to this reaction enthalpy (the entropy is not known), then the thermodynamic cycle shown in equation [4.9] can be used to estimate the potential required to leach brannerite (incongruently):

$$V_{Brannerite/UO_2^{2+}} = \frac{\Delta G_{(Brannerite/UO_2)}}{-vF} + V_{UO_2/UO_2^{2+}} \qquad [4.9]$$

The first term on the right hand side of equation [4.9] will basically appear as a contribution to the energy barrier. Assuming that the influence of potential on the reaction rate is exponential (as one expects from the Butler-Volmer kinetics), it was calculated that the relative rate of leaching of brannerite, versus uraninite, on the basis of the increase in required potential due to the extra term in equation [4.9] is such that the rate of leaching of brannerite is 16.1 times slower than the rate of leaching of uraninite at 60°C. This theoretical figure is in agreement with the findings by Zhang *et al.* [2003] that the rate of uranium release from brannerite is an order of magnitude lower than release from UO_2. Therefore, slightly longer residence times and a higher potential may be required to

increase the extent of brannerite dissolution at the same aera exposure as uraninite. It is proposed that the requirements to leach brannerite are attainable within the usual window of operation for atmospheric leaching, provided that the mineral is sufficiently exposed. Results from increasing the potential (using nitric acid) showed that dissolution of uranium is not improved beyond 90 %. Extending the leaching time to 48 hrs resulted in similar levels of dissolution as at the low pH conditions (see Table 4.14).

Table 4.14: Uranium dissolutions after 48 hrs of leaching (aggressive leaching conditions)

Ore Type	U Dissolution (%)
Kopanang	93.3
Noligwa	89.9
Moab Khotsong	91.3

The fact that the largest fraction of unleached uranium present in the residue exists as brannerite is an indication of the slow reaction kinetics of brannerite. From the results discussed it seems that brannerite leaching is limiting optimum recovery. The brannerite minerals are exposed to the leaching environment. Therefore, is it necessary to determine conditions which will increase brannerite's kinetics. It must be possible to extend brannerite dissolution by employing extreme leaching conditions (e.g. pressure leaching at high potentials and temperature). A simple doubling of residence time to 48 hours and use of nitric acid were not effective. Instead of trying to guess conditions, it is recommended to follow a diagnostic leaching approach. Through diagnostic leaching it will be possible to better understand the leaching kinetics of the different minerals and to determine is it is possible as well as economically viable to increase uranium recovery beyond 90 %. Chapter 6 explains the diagnostic leaching method as well as the results obtained. It is however possible to calculate the required conditions from a kinetic model that has a sound basis. In Chapter 7, a method to develop such a model is proposed.

4.2.5 Reagent Consumers

Results showed that Kopanang ore consumes less acid, as compared to the other ores. Appendix B - Section 11.8 contains tables of the mineralogy of the residue samples which must be compared to the bulk mineralogy to establish the reason for different acid consumption behaviour for the ores. From the mineralogical analysis, it seems that quartz, muscovite, pyrophyllite and albite are not major acid consumers, while chlorite seems to be a major acid consumer. Pyrite is an acid producer, reacting with ferric in solution to form ferrous and acid. The lower chlorite concentration in Kopanang ore is thought to be partly responsible for the lower acid consumption. Although chlorite is an acid consumer, it is also an iron producer, providing the necessary iron for uranium leaching before the addition of a solid oxidant.

Another important point to note from Table 4.6 is that the total acid consumed by Kopanang ore, for a given set of conditions, is lower than the acid consumption by the other ores. This implies that Kopanang ore has a lower proportion of acid consuming constituents. Also, acid consumption increases with acid addition for all ores. This is expected, as the rate of acid-consuming reactions should initially be a function of the acid concentration in solution as long as the reactions are acid limited. Practically, this has implications on the method that should be used to add acid to the ore (single-point addition vs. control of a free acid level through-out the leach train).

For oxidant requirements, pyrolusite is mostly used in the mining industry, since it is inexpensive. MnO_2 has the thermodynamic potential to oxidise U^{4+}, but since it is kinetically difficult for a solid to oxidise another solid, manganese dioxide works via iron (Fe^{2+}). Before introducing additional iron to the system it is important to establish if the iron content in the ore is sufficient or not. Addition rates for pyrolusite should be based on the expected concentration of iron in solution, according to the idealised chlorite reaction (there could be other chlorite forms):

$$Mg_2Fe_2Al_{3.3}Si_{2.5}O_{10}(OH)_8+4H_2SO_4 \leftrightarrow 2Mg^{2+}+1.7Fe^{2+}+0.3Fe^{3+}+3.3Al^{3+}+4SO_4^{2-}+2.5SiO_4^{2-}+8H_2O \quad [4.10]$$

If calcine (a mixture of magnetite and hematite) is introduced as a source of iron(III), replacing pyrolusite, the precise composition of the calcine must be known. If the concentration of hematite is very low then the decision must be reconsidered as calcine is a large acid consumer, which will increase iron in solution but not necessarily as Fe^{3+}. A calcine leach solution sample showed low Eh values which are indicative of a small Fe^{3+}/Fe^{2+} ratio. Therefore, calcine as a pyrolusite replacement has to be considered with care (especially in terms of its effect on solution potential and acid consumption). It is also noted that the particular calcine sample (2670 ppm U) under aggressive leaching conditions (Temp: 60°C, H_2SO_4: 25 kg/t) gave a uranium dissolution of merely 36 %.

4.2.6 Uranium dissolution trends of Pilot Plant Scale Tests

The previous mentioned results are from laboratory scale tests. However, the question still remains if the same trends can be recognised for plant scale tests. Results from a pilot plant trail (done by AngloGold Ashanti at the West Uranium plant) were received for the period 13 September 2005 – 12 October 2005 treating Kopanang residue samples. The results are presented in Figure 4.10. The graph contains the following information: The red dotted area represents the maximum amount of uranium that will be available in solution given the initial acid and temperature based on the model developed by Bonthuys and Mhlungu [2005] (Equation [4.8]). The dark blue represents the maximum calculated uranium in solution using the head grade while the light blue is the actual amount uranium leached. From this graph it is clear that uranium extraction is definitely not under solubility limitations. Note that the acid addition drastically decreased after the 27 September 2005.

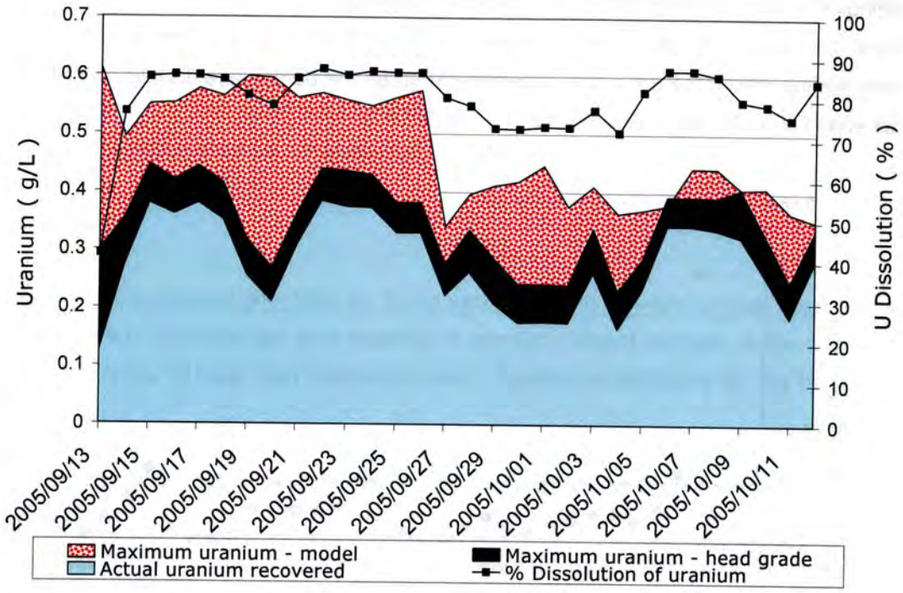

Figure 4.10: Uranium dissolution results of pilot plant tests for Kopanang ore

Figure 4.11 shows the effect of the different acid concentration of the dissolution of uranium. It can be noted that at high acid addition the range of dissolution is much smaller than at low acid concentration. The interesting part though is that the percentage dissolution never exceeds 88% no matter the acid concentration. This supported the theory that more aggressive leaching (over dosage of acid) is not capable to fully extract uranium and that leaching is definitely under mineralogy limitations.

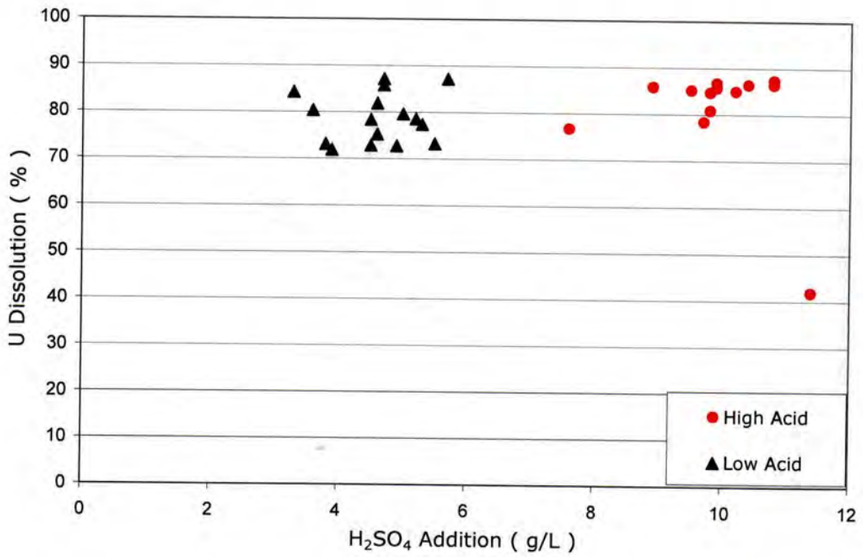

Figure 4.11: Effect of acid concentration on the dissolution of uranium

Something else to note (from Figure 4.10) is that there is a definite correlation between the head grade and the amount of uranium recovered. It seems that the unleachable uranium in absolute terms must very similar seeing that for a decrease in head grade the percentage dissolution of uranium also decreases and is confirmed in Figure 4.12.

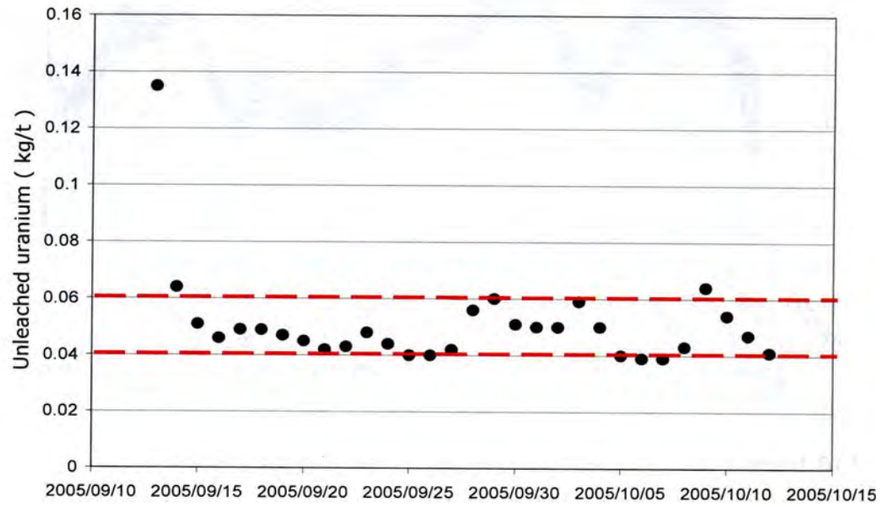

Figure 4.12: Fraction of uranium not leached

This is similar to findings of Ford and Gould [1994] stating that the absolute amount of inert uranium is a fix amount. The only difference is in the absolute amount of unleachable uranium which vary between 0.04 kg/t and 0.06 kg/t and not 0.015 to 0.030 kg/t as according to Ford and Gould.

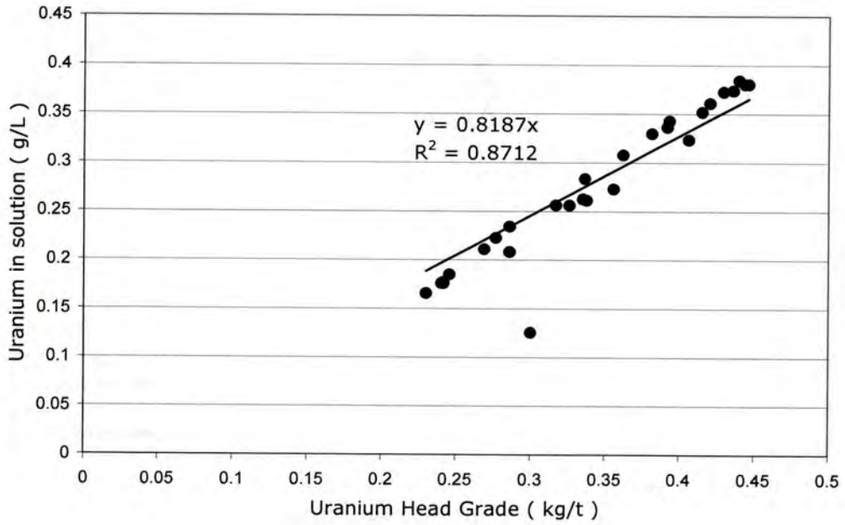

Figure 4.13: Uranium in solution vs. head grade

After further evaluation of the data it became evident that varying the different leaching parameters has very little to no effect on the percentage uranium leached. From the graph in Figure 4.13 can be seen that independent of the conditions or reagent dosages, 81.87% of the uranium is recovered. The results from both the pilot plant scale tests as well as the laboratory scale point to the same conclusion that the uranium extraction must be mineralogically limited.

4.3 Summary

It was found that dissolutions higher than 90 % are very difficult to achieve for Vaal River ores under the normal window of operation for acid leaching of uranium, except perhaps at the uneconomical extremes (e.g. very low pH and high residence times). Possible explanations for the existence of a maximum include:

- Mineralogical limitation, specifically slow leaching kinetics of brannerite (most likely explanation).
- Limitations due to maximum solubility of uranium having been reached (highly unlikely explanation).
- Other forms of diffusion control (external mass transfer unlikely to affect terminal dissolutions, may affect initial rates. Internal diffusion likely, but mode of particle breakage may give unconventional trends).

Of the variables that were investigated, acid addition was found to have the greatest influence on terminal dissolutions. At 60ºC, 4 kg/t MnO_2 addition, and 16.3 kg/t sulphuric acid addition, dissolutions of 80 % can be taken as safe technical numbers for Moab Khotsong and Great Noligwa. 85 % uranium extraction can be expected for Kopanang. These results are in contradiction to Ford and Gould's theory which stated that the higher the grade the higher the percentage recovery since the amount of unleachable uranium minerals is constant.

Under these conditions, acid consumptions are 11.2, 13.9 and 15.9 kg/t for Kopanang, Great Noligwa, and Moab Khotsong ores, respectively. During plant operation, consistent tank hydrodynamics will need to be maintained to ensure that the dissolutions are sustainable. Under the normal operating window, i.e. not considering uneconomical leaching conditions, ~ 90 % dissolution will be a maximum. Aggressive leaching conditions as defined in this report are thought to be suitable for achieving maximum value from an atmospheric leach set-up. If ~ 100 % extraction is desired, more extreme conditions (probably pressure leaching) will be necessary. Since the chlorite reaction produces ferrous and ferric ions, the strategy for addition of pyrolusite (which, in addition to MnO_2, was thought to provide Fe) has to be revisited, as there may be scope for a significant reduction in its addition. This is more so in the light of the low sensitivity of the terminal dissolutions to MnO_2 addition (as long as sufficient acid is added). It may be worthwhile calculating the MnO_2 requirement based on a multiple of the stoichiometric requirement of the ferrous generated in the first 1 or 2 hrs of the reaction.

Chapter 5

Forward and Reverse Uranium Leaching

The Vaal River Region is part of the Witwatersrand Basin which is host to the world's largest gold deposit; at an average grade of 9.5 g/t. In the Witwatersrand Basin, gold is generally associated with uranium. When uranium prices are low, the benefit is primarily due to the extra unlocking of gold following an acid pre-treatment during uranium leaching, but when uranium prices are high the value of the uranium by-product also adds significantly to the benefit.

Although uranium is becoming an increasingly favourable commodity for producers, due to the increasing demand, it is still viable only as a by-product of gold production (in the Vaal River context). The process of extracting gold differs from the process of extracting uranium. With respect to gold extraction, two process routes can be considered: (i) forward leaching (direct cyanide leaching of gold) and (ii) reverse leaching (sulphuric acid leaching of uranium followed by cyanide leaching of gold). It has been known for some time that the ultimate gold recoveries for the two routes differ, with the reverse leach usually yielding more gold. The aim of this chapter is to examine these two options in more detail and to quantify the anticipated benefit for reverse leaching.

5.1 Experimental Details

The same sample preparation procedure was followed as described in Section 4.1.1.

5.1.1 Forward Leaching

Forward leaching refer to direct cyanide leaching. The leaching experiments were carried out in 2L water-jacketed batch reactors which were mechanically agitated. A pulp mixture consisting of 1310 g of the dried milled sample (80 % -75 µm) and 1015 mL water was preheated to 30°C. The pulp was agitated at 6 rpm to fully suspend the solids. The pH of the pulp was adjusted by additions of small amounts of lime, typically 0.1 g at a time, using a spatula. The initial pH was set to ~10.5. Before NaCN was added to the reactor, air was manually sparged. The air sparger was assembled with the baffle and left in the reactor till the end of the test. The test commenced after the addition of 0.65g

NaCN (~347 mg/L CN^-). Slurry samples of 170 mL were collected and filtered at sampling times 2, 4, 6, 8 and 24 hours. The solids were tested for Au concentration while the solutions were analysed for [Au], [CN^-] and [Fe]. Tests were performed in duplicates.

5.1.2 Reverse Leaching

Reverse leaching entails uranium leaching followed by gold leaching. For uranium leaching the pulp mixture consisting of 1310 g ore (80% - 75µm) and 1015 ml water was pre-heated for 1 hr to the test temperature (50°C) for uranium leaching, before the start of each experiment. Sulphuric acid (26 ml of 647 g/L sulphuric solution) was added to the mixture, signifying the start of the experiment. After 1.5 hours, the solid oxidant (12 g of pyrolusite) was added. The residue after 24 hours was filtered and dried. It is important to minimise ore losses. A pulp mixture that is made up of the dried ore and water (solid:water ratio of 1.55) and placed in another 2 L water-jacketed batch and was preheated to 30°C. The pulp was agitated at 6 rpm to fully suspend the solids. The pH of the pulp was adjusted by additions of small amounts of lime, typically 0.1g at a time, using a spatula. The initial pH was set to ~10.5. Before NaCN was added to the reactor, air was manually sparged. The air sparger was assembled with the baffle and left in the reactor till the end of the test. The test commenced after the addition of 0.65g NaCN (~347 mg/L CN^-). Slurry samples of 170 mL were collected and filtered at sampling times 2, 4, 6, 8 and 24 hours. The solids were tested for Au concentration while the solutions were analysed for [Au], [CN^-] and [Fe]. Tests were performed in duplicates.

5.2 Results and Discussion

5.2.1 Gold Recovery

A summary of the gold residue grades after 8 and 24 hour of leaching are presented in Table 5.1 for both forward and reverse leaching.

Table 5.1 Gold residue grades for the forward and reverse leach method for 8 and 24 hours.

	Au Residue Grade (g/t)				
	Forward Leach		Reverse Leach		Δ
	8 hrs	24 hrs	8 hrs	24hrs	24hrs
Kopanang	0.77	0.48	0.185	0.12	0.36
Kopanang (Duplicate Test)	0.71	0.64	0.28	0.13	0.51
Noligwa	1.00	0.69	0.32	0.27	0.42
Noligwa (Duplicate Test)	0.86	0.675	0.36	0.23	0.445
Moab Khotsong	0.97	0.93	0.67	0.31	0.62
Moab Khotsong (Duplicate Test)	0.84	0.71	0.38	0.28	0.43

In the table, Δ is the difference in residue gold grades between the forward and reverse leach methods after 24 hours. Solid analyses are used for interpretation in all cases. From the results it is clear that reverse leaching, when applied on the bulk ore, improves gold extraction by between 0.4 and 0.6 g/t. This suggests that reverse leaching does indeed unlock some refractory gold. Sulphuric acid destroys some of the gangue minerals with which some of the gold is associated, liberating the gold and thus leading to higher recoveries. In Figure 5.1 and Figure 5.2, the effect on the total recovery of gold can be seen. Note that these findings should not necessarily be generalised to concentrates.

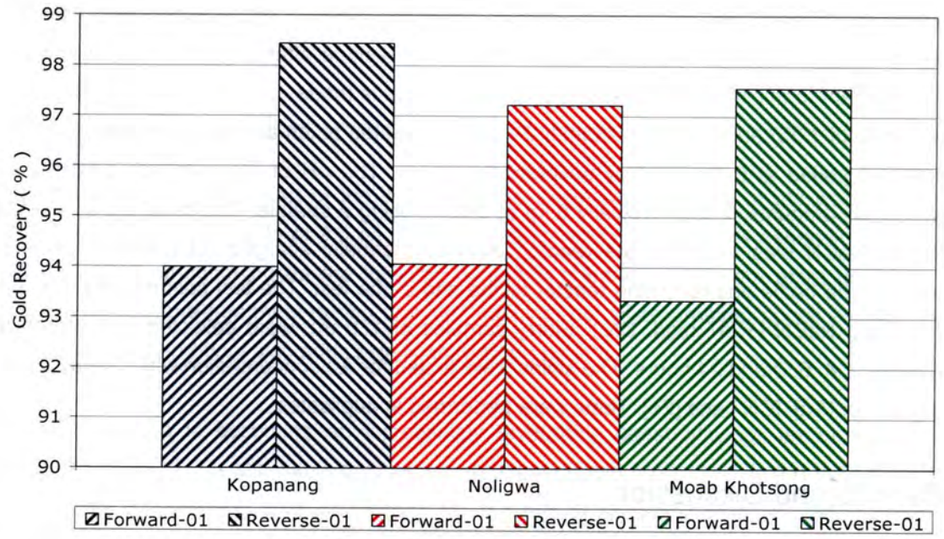

Figure 5.1: Gold recovery for forward leach vs. reverse leach

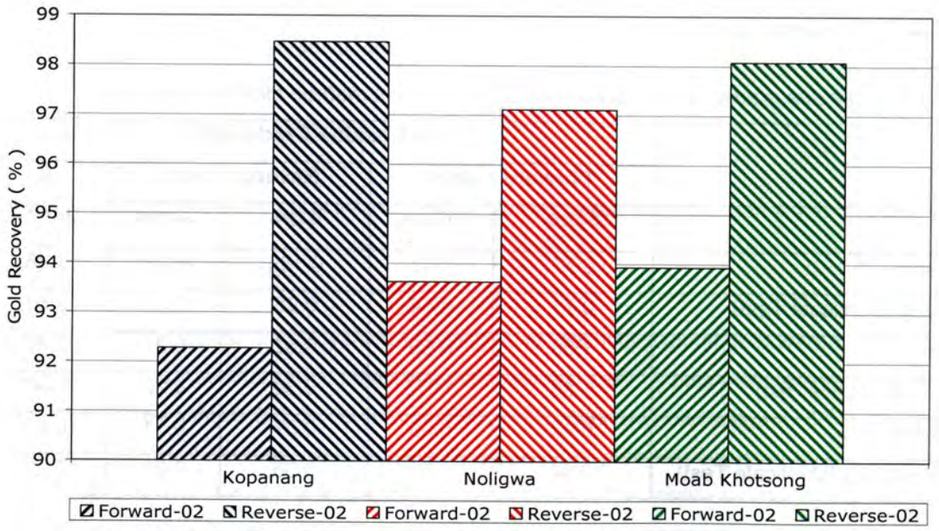

Figure 5.2: Gold recovery for forward leach vs. reverse leach (Duplicate Test)

The benefit of reverse leaching in general is an increase in total gold recovery of between 3 and 4 percentage points for the three ores, making gold recoveries as high as 98 % possible.

5.2.2 Cyanide Consumption

Cyanide consumption data using the two different methods are presented in Figure 5.3 and Figure 5.4.

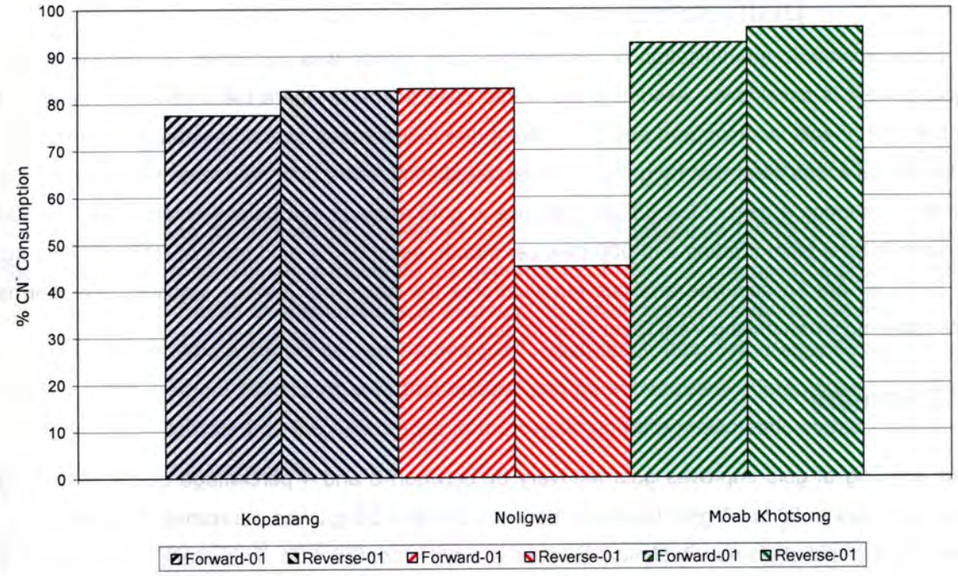

Figure 5.3: Cyanide consumption for forward and reverse leaching tests for the 3 ores

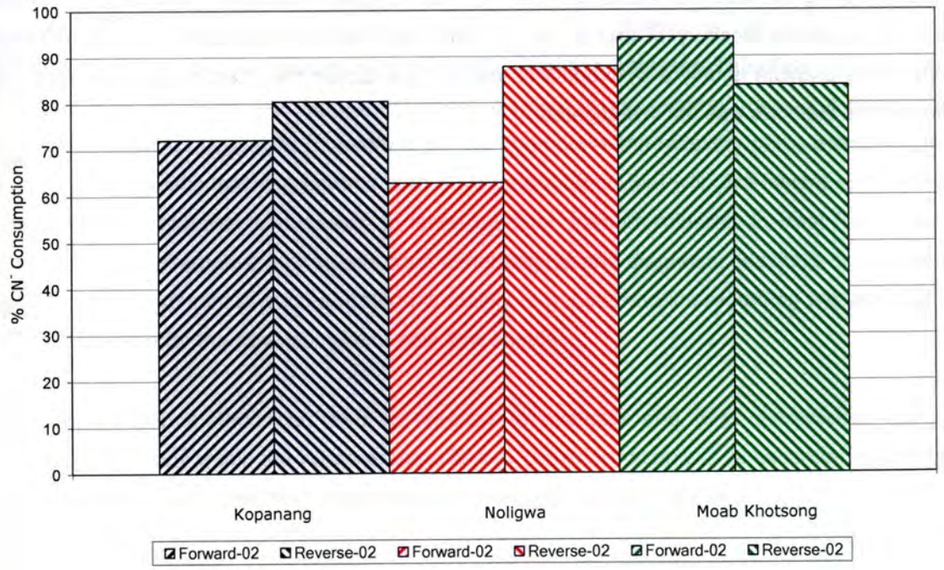

Figure 5.4: Cyanide consumption for forward and reverse leaching tests for the 3 ores (Duplicate Test)

From the graphs there are no specific trends. This could suggest that the true differences in cyanide consumptions are minor, possibly below the combined experimental and analytical errors. More accurate determinations are required if any definite conclusions are to be drawn. However, since in practice a common dosage will be employed, it was not found necessary to investigate this issue at any great length.

5.2.3 Economic Analysis

A very crude economic quantification of the reverse leach option was performed for completeness. Only gold benefit is considered, assuming the worse case scenario where the uranium revenue just equals the cost of acid leaching and any lost interest due to increased overall residence time for gold. From the results it was clear that by going for reverse leaching, extra gold recovered lies between 0.4 and 0.6 g/t. Assuming a gain of 0.4 g/t, the increase in gold revenue can be estimated to be R14 400 000 per month for a plant treating 240 000 tons per month, assuming a gold price of R150 000 per kg. This is probably not an accurate analysis but illustrates the point that reverse leaching operation is worth considering when mining Vaal River ores for gold.

5.3 Summary

Reverse leaching of gold improves gold recovery by between 3 and 4 percentage points, improving total gold recovery to 98 %. A gold benefit of between 0.4 and 0.6 g/t was measured. This result was expected, and in this short note technical reasons are not elaborated on. The exact financial gain is dependant on the gold price and other economic factors, but an estimated benefit for treating an average of 240 000 t ore/month is in the order of R 14 000 000/month (in terms of gold leaching only). The reverse leaching operation for recovery of both gold and uranium is therefore a financially justified process route, because recovery of uranium will ensure that the costs are lower than the revenue increment. Since uranium is only a by-product of the gold production the effect on uranium recovery using the various methods was not investigated

Chapter 6

Uranium Diagnostic Leaching

Diagnostic leaching as defined by Tumilty *et al.* [1986] and Lorenzen [1992] is a simple series of sequential leaches developed to elucidate the deportment of minerals containing a specific element in various matrices. Based on a mineralogical examination, which quantitatively determines the minerals present in the matrix, a sequence can be designed. Each leach destroys a specific mineral and the amount of the element associated with that mineral can be subsequently determined. The method is developed on the basis that the differences in the kinetic and thermodynamic stability of the various minerals allow leach selectivity.

In practice, as also seen in literature, uranium recovery higher than 90 percent is seldom achieved for South African ores (refer to Table 2.6). To establish the reasons for the difficulty in achieving higher uranium dissolutions, a diagnostic leaching method can be used to analyse the unlocking and dissolution of refractory uranium. The development of this method will be explained in detail in this chapter. With some current technologies it is possible to determine the amount of an element associated with a specific mineral using a mineral liberation analyser. Therefore, the question is not necessarily to determine the deportment of the element in the mineral matrix but rather conditions necessary to leach the specific minerals to be able to improve the recovery of the element. The aim of a uranium diagnostic leaching method is to develop a method that will give insight as to whether it is possible, within practical boundaries, to leach residual uranium minerals in Vaal River ores and to possibly design alternative flow sheets from mineralogical and diagnostic leaching data. Note that the aim of the development of such a method is mainly to get information regarding the leaching process that can be used for the development of new flow sheets.

This step-by-step method can also be applied to evaluate and fully characterise any uranium containing ore body within the Witwatersrand Basin. The information will be essential regarding choice of leaching technique, operating conditions and expected uranium recovery.

6.1 Experimental Details

6.1.1 Structural Planning of Design

When designing a diagnostic leaching method it is important to start with the necessary information regarding the ore (i.e. mineralogy, liberation, surface area exposure, residue mineralogical analysis etc.) that is treated (refer to Chapter 3). A diagnostic leaching method was originally designed for gold leaching. Gold is captured in the gangue minerals, therefore, the diagnostic leaching method involves selective oxidative leaching to destroy gangue minerals liberating the gold [Lorenzen, 1992], which is then dissolved in an alkaline cyanide solution. Since gold only dissolves in cyanide it is easy to set leaching boundaries.

For uranium leaching, the bulk mineralogy studies in Chapter 3 have shown that dissolution is not necessary caused by entrainment (very high surface exposure of the different uranium minerals). The residue analysis also showed that basically all the uraninite had dissolved in the leaching experiments and that most of the unleached uranium is brannerite which is at least exposed and some of it fully liberated. Based on that, it is not really necessary to use a diagnostic leaching method to unlock the refractory uranium mineral since it is already exposed. In this context it is more important to determine the conditions necessary to leach the uranium – by employing increasingly aggressive leaching conditions.

In the ore samples that have been tested it is known that the uranium minerals present are: uraninite, brannerite, coffinite and U-phosphates. The conditions to dissolve uraninite are well known from literature. It is also known that coffinite is less reactive than uraninite while brannerite is less reactive than coffinite and U-phosphates are expected to be inert. At this stage there is little knowledge with reference to brannerite leaching – although it is known to be very inert. In literature it is reported that the reaction rate of brannerite reactivity is a magnitude slower compared to uraninite's rate [Zhang *et al.*, 2003]. This means that in order to leach brannerite more aggressive leaching conditions need to be employed (refer to Chapter 4 – Section 4.2.4).

6.1.2 Experimental Procedure

6.1.2.1 Residence Time

Since it is known that brannerite has slow leaching kinetics the first step was to determine if uranium leaching is not limited by time (that it just takes a long time to leach). The dependency of total uranium recovery were evaluated at different residence times supplying the necessary potential as well as acid concentration over the leaching period. The leaching tests were carried out at aggressive plant conditions (Temperature: 60°C, H_2SO_4: 16.3 kg/t, MnO_2: 4 kg/t).

The leaching experiment was carried out in a 2L water-jacketed batch reactor, which was mechanically agitated. Sulphuric acid was added as a 647 g/L H_2SO_4 solution. Pyrolusite containing 29.3 % MnO_2 and 36.5 % Fe was used as a solid oxidant. The absolute dosages were calculated on the basis of a pulp RD of 1.55 and a solids SG of 2.7. Stirring speed was kept constant at 6 rpm. The experiment was divided into 3 tests which run sequentially over 72 hours. The standard working procedure followed is described in Appendix B – Section 11.1.

The experiment start with a pulp mixture consisting of 1310 g ore and 1015 ml water was pre-heated for 1 hr to the test temperature, before the start of the experiment. Sulphuric acid was added to the mixture at time t=0, signifying the start of the experiment. After 1.5 hours, the solid oxidant (pyrolusite) was added. After 24 hours the experiment was stopped and filtered. The solids were dried and a sample was taken. The solutions were analysed for $[U^{6+}]$, [Fe], $[Fe^{2+}]$, $[Mn^{2+}]$ and $[H^+]$, while solids were analysed for U and Fe only. Solids were also sent for mineralogical analysis. The remaining solids were used for the next experiment. This was repeated 3 times up to a total of 72 hours. Each time the same procedure was used as described above. Enough water was added to ensure the same solid:water ratio and the acid and manganese dioxide amount was calculated accordingly.

6.1.2.2 Potential

Different lixivants give different results due to potential provided by the reactions taking place, acid concentration as well as changes in stability constants of the uranyl association complexes with different ligand anions. According to Abdel Razik *et al.* [1988] the order of decreasing complexing power of different anions on uranium is as follows: $F^- > SO_4^{2-} > Cl^- > Br^-$. This complexing factor refer to the affinity of uranium species in solution to form a complex with the respective anions; moreover the potential necessary to bring the uranium into solution is still required which are not necessarily provided by the lixiviant.

The aim of these tests is to manage the potential using an auto titrator ensuring a constant potential throughout the process eliminating the possible effect of variation in potential. Firstly, a test was done only at natural Eh (only adding H_2SO_4, no oxidant). Thereafter two tests were performed, accelerating leaching by setting the potential at 500 mV (vs. SCE) and 700 mV (vs. SCE) using H_2O_2 and HNO_3, respectively.

The leaching experiment was carried out in a 2L water-jacketed batch reactor, which was mechanically agitated. An auto titrator as well as a data collector (see experimental setup in Figure 6.1) was used to control the oxidant addition and capture the relevant information. Note that an anti oxidant was not used therefore if the potential overshoot only the reaction will bring it back to the set potential. The experiment starts with a pulp mixture consisting of 1310 g ore and 1015 mL water. Sulphuric acid (33 mL of 647 g/L H_2SO_4) was added to the mixture before heating the solution to 60°C. A 30 minutes delay after the addition of the acid and before the oxidant was added allowing time for the potential of the system to stabilise before the oxidant was added to pre-dose the solution to the set

potential. Thereafter, the experiment started for the duration of 24 hours. After 24 hours the experiment was stopped and filtered. The solids were dried and a sample was taken. The solutions were analysed for [U^{6+}], [Fe], [Fe^{2+}], [Mn^{2+}] and [H^{+}], while solids were analysed for U and Fe only. Solids were also sent for mineralogical analysis. The standard working procedure summarised in Appendix B – Section 11.1 was followed.

Figure 6.1: Experimental setup using the auto titrator

6.1.2.3 Extreme Leaching conditions

Using the residue from sulphuric acid leaching with no addition of oxidant, extreme conditions can be used to determine if it is possible to dissolve the remaining uranium minerals (specifically brannerite). Over dosing of nitric acid combined with high temperature were investigated. The following method was used as proposed by Lorenzen [1995]:

Nitric acid mostly reacts with sulphates and the reaction is highly volatile and envolves dangerous brown fumes of NO_2. The leach must be carried out in a well ventilated fume cupboard and the nitric acid should be added slowly to the agitated slurry before heating.

A stock solution of 1:1 HNO_3 (55%)/distilled water by volume was added to a beaker containing the filtered wet solids to make up to roughly 10:1 L/S ratio. The mixture was boiled for 6 hours or until no further reaction occurs (i.e. no brown fumes of NO_2 evolve). Additional HNO_3 was added to make up for evaporation losses. At the end of the leach the solids were filtered and washed using distilled water (to a L/S of about 2:1). Repeat this step at least two times. The filtrate of the NO_3 leach was sent for analysis to determine the uranium concentration as well as the residue sample to determine if there is any uranium left.

Figure 6.2: Experimental setup for nitric acid leaching tests

6.2 Results and Discussion

Firstly tests were done without the addition of an additional oxidant primarily to remove all the "easy" leaching uranium minerals (not forcing uranium leaching to take place). In addition to the results obtained it was possible to determine the true influence of an additional oxidant. Uranium dissolution results for sulphuric acid leaching at natural potential (without the addition of an additional oxidant – potential ranges are defined in Table 6.1) are as follows (note that the potential was measured at reaction temperature):

Table 6.1: Results of sulphuric acid leach without an additional oxidant (Acid: 16.3 kg/t; Temp: 60 °C)

	Minimum Eh (mV vs. SCE)	Maximum Eh (mV vs. SCE)	Average Eh (mV vs. SCE)	U Dissolution (%)
Kopanang	390.9	450.1	415.9	83.6
Noligwa	371.7	465.7	411.7	82.1
Moab Khotsong	287.1	457.5	359.2	81.7

From Table 6.1 it is clear that the initial potential (provided by the Fe that is leached from the ore) is sufficient for uranium leaching to take place under aggressive acid leaching conditions. It is important to note the Fe^{3+} in the ore serves as an oxidant, the absence of MnO_2 only result in no regeneration of Fe^{2+} to Fe^{3+}. Therefore, dissolutions over 80 % are not unusual regardless of the absence of an additional oxidant. For Kopanang and Noligwa ore the potential drop over a 24 hour period to below 400mV but average over the leaching period 416 and 412 mV, respectively. For Moab Khotsong the change in Eh was more severe averaging only 359 mV. From the Nernst equation, potential is a function of the Fe^{3+}:Fe^{2+} ratio therefore, the lower Eh maybe attributed to the fact the Moab Khotsong ore contains more chlorite and pyrite. It is found that the actual Fe^{3+} concentration maybe more

important than the actual potential that are illustrated in Table 6.1. To compare the absolute contribution of the addition of an oxidant, dissolution results with oxidant addition and without are presented in Table 6.2.

Table 6.2: Leaching results comparing the difference with and without the addition of a oxidant

	U Dissolution (%) with oxidant	U Dissolution (%) without oxidant
Kopanang	90.3	83.6
Noligwa	83.5	82.1
Moab Khotsong	80.5	81.7

Adding the same amount of acid, results form Table 6.2 indicate that the iron (Fe^{3+}) supplied by the ore is sufficient and that the addition of a oxidant (increasing the Fe^{3+} concentration and directly increasing the potential) did not have a significant effect on the total dissolution of uranium from Noligwa and Moab Khotsong ore. However, the addition of the oxidant did seem to have an effect on the uranium dissolution form Kopanang ore. These results can be explained in terms of the bulk mineralogy of the different ores (Chapter 3 - Table 3.1). Noligwa and Moab Khotsong ore contains a significant amount more chlorite which provide both Fe^{2+} and Fe^{3+}. It also contains more pyrite, consuming Fe^{3+} and produces Fe^{2+}. Therefore, as indicated in Table 6.1, the overall potential maybe lower (due to a higher concentration of Fe^{2+}) but maybe the absolute amount of Fe^{3+} is sufficient for uranium leaching. Interpreting the results it became evident that the addition of an oxidant may not be that critical in leaching Noligwa and Moab Khotsong ore and the opposite for Kopanang ore. This indicates that there is definite scope for reduction of additional oxidant and that further investigation in this regard is needed.

Leaching with sulphuric acid and manganese dioxide is operating conditions that are attainable on plant scale and in Chapter 4 it was shown that independent of the conditions it was not possible to increase the uranium dissolution beyond 90 %. To establish if it is possible to increase the total uranium yield it is necessary to move outside operating boundaries. Previous work done by Lorenzen [1992] showed that there is not a big difference in the total uranium dissolution between leaching at 400 mV and 600 mV (vs. SCE). Based on that, it was decided to do tests at 500 mV and 700 mV (vs. SCE). Leaching with sulphuric acid and manganese dioxide it is impossible to increase the overall potential above 500 mV (vs. SCE). Therefore, it was necessary to use H_2O_2 and HNO_3 to reach higher potentials. For the H_2O_2 tests sulphuric acid was also added to maintain a reasonable pH within the thermodynamic window. Nitric acid is both a strong acid as well as a high oxidising agent; therefore, for the nitric acid test no sulphuric acid was added. The pH values after 24 hours are reported in Table 6.3. Since different oxidants were used it will only make sense to compare end dissolutions.

Table 6.3: pH values of constant Eh tests

	500mV	700mV
Kopanang	1.08	0.55
Noligwa	1.57	1.07
Moab Khotsong	1.52	1.21

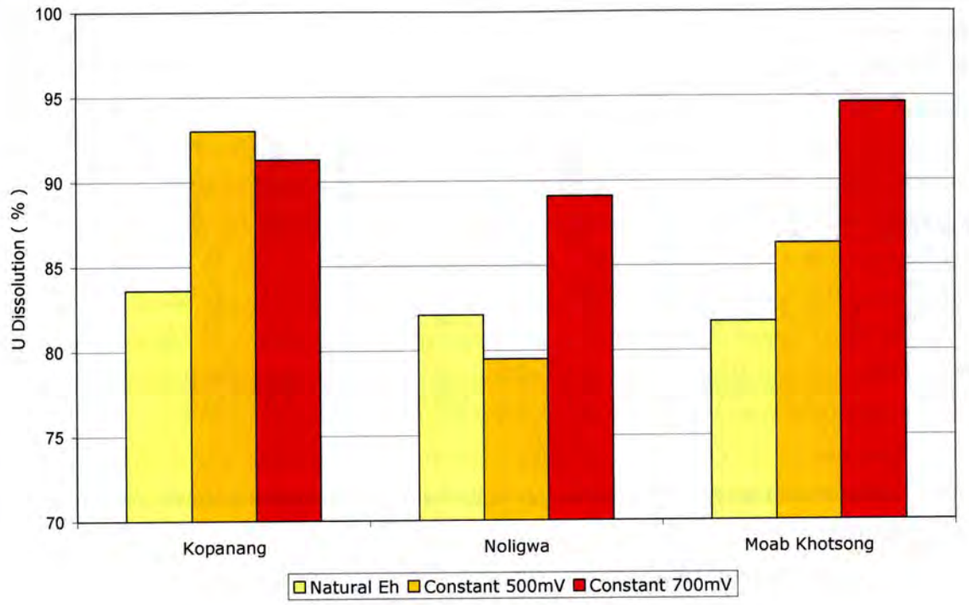

Figure 6.3: Comparing uranium dissolution at different constant potentials

From Figure 6.3 it can be seen that there is a significant increase in the uranium dissolution for Kopanang ore moving form 300 mV to 500mV but no increase upon increasing the solution potential to 700mV. It is possible that maximum leachable uranium has leached. However, for Noligwa and Moab Khotsong ore there were improvements of between 8 and 10 basis points leaching at 700 mV. Interestingly it was found that variation of potential have a great effect on the dissolution of uranium for Kopanang ore at lower potentials (see Table 6.2) while it only start to show to have a significant effect on dissolution at higher potential for Noligwa and Moab Khotsong ore. The reason is probably due to mineralogical influences. Evaluating the bulk mineralogy it is possible to partly explain these results in terms of the sulphide mineral composition of these ores. Kopanang ore contains little pyrite while Noligwa and Moab Khotsong contain significant higher amounts as previously mentioned (see Chapter 3). Increasing potential for 500 mV to 700 mV destroy these sulphide minerals liberating the uranium associated with these minerals. In the case of Kopanang the majority of uranium minerals left after natural Eh leaching is brannerite which show very slow leaching kinetics, thus only slight increase in extraction. The uranium distribution of the residue uranium indicated that the main uranium minerals left is brannerite. However, since the uranium concentrations left are very low the results are rather expressed as absolute uranium deportment of the different uranium minerals left (in ppm) to put the results more in perspective (see Table 6.4 – Table 6.6). Since the uranium concentration in uraninite is much higher compared to brannerite, higher absolute uranium concentrations left as uraninite compared to brannerite is expected. Also note that the mineralogy results are relative and only give an indication since the samples only contain trace amounts of uranium.

Table 6.4: Uranium mineralogy (expressed as ppm) for the residue samples Kopanang ore after tests at different potentials

	Natural Potential			500mV			700mV		
Kopanang	Start (ppm)	Left (ppm)	Dissolved (%)	Start (ppm)	Left (ppm)	Dissolved (%)	Start (ppm)	Left (ppm)	Dissolved (%)
Uranium	234.1	38.3	83.6	357.3	24.9	93.0	243.6	21.2	91.3
Uraninite	198.8	25.1	87.4	303.3	18.1	94.0	206.8	17.0	91.8
Brannerite	30.2	10.9	63.8	46.1	6.2	86.5	31.4	4.2	86.7
U_Phosphate	0.5	0.5	0.0	0.7	0.6	10.3	0.5	0.0	100.0
Coffinite	4.7	1.1	76.0	7.1	0.0	100.0	4.9	0.0	100.0

Table 6.5: Uranium mineralogy (expressed as ppm) for the residue samples Noligwa ore after tests at different potentials

	Natural Potential			500mV			700mV		
Noligwa	Start (ppm)	Left (ppm)	Dissolved (%)	Start (ppm)	Left (ppm)	Dissolved (%)	Start (ppm)	Left (ppm)	Dissolved (%)
Uranium	320.5	57.2	82.1	306.6	62.8	79.5	353.8	38.5	89.1
Uraninite	255.4	47.1	81.6	244.4	47.0	80.8	282.0	29.5	89.5
Brannerite	59.3	10.1	83.0	56.7	15.8	72.2	65.5	9.0	86.3
U_Phosphate	0.3	0.0	100.0	0.3	0.0	100.0	0.4	0.0	100.0
Coffinite	5.4	0.0	100.0	5.2	0.0	100.0	6.0	0.0	100.0

Table 6.6: Uranium mineralogy (expressed as ppm) for the residue samples Moab Khotsong ore after tests at different potentials

	Natural Potential			500mV			700mV		
Moab Khotsong	Start (ppm)	Left (ppm)	Dissolved (%)	Start (ppm)	Left (ppm)	Dissolved (%)	Start (ppm)	Left (ppm)	Dissolved (%)
Uranium	444.9	81.6	81.7	475.3	65.2	86.3	649.4	34.5	94.7
Uraninite	396.9	56.2	85.8	424.0	42.2	90.1	579.3	26.0	95.5
Brannerite	34.3	24.3	29.0	36.6	22.1	39.7	50.0	8.5	82.9
U_Phosphate	1.8	1.1	37.4	1.9	0.9	52.2	2.6	0.0	100.0
Coffinite	12.0	0.0	100.0	12.8	0.0	100.0	17.5	0.0	100.0

From Table 6.4 – Table 6.6 the following where noted: The uranium contribution in the leaching solution from brannerite is very little compare to uraninite. The increase in uranium dissolution by an increase in the potential is mostly due to an increase in the dissolution of uraninite. Brannerite and uraninite is associated with each other. It is speculated that destroying gangue minerals as well as dissolving some brannerite, liberate remaining uraninite particles, thus increasing uraninite dissolution (brannerite's associations table is included in Appendix D). Brannerite kinetics is expected to be very slow but there is a definite increase in brannerite dissolution for Noligwa and Moab Khotsong at more aggressive leaching conditions moving to 700 mV (see Table 6.5 and Table 6.6). Leaching at more oxidising conditions results in the dissolution of sulphate minerals which are probably the reason for the increase, since brannerite is highly associated with pyrite (see Appendix D for associations). These experiments proved that even under such extreme conditions it was not possible to get a total dissolution. Table 6.7 and Table 6.8 indicate that the remaining uraninite and brannerite is to a large degree exposed to the leaching environment. To determine the effect on the leaching kinetics of brannerite, it is recommended to do tests at longer leaching times at 700 mV since the recovery of Noligwa and Moab Khotsong ore still on the increase.

Table 6.7: Percentage brannerite liberation and percentage of brannerite with 5 and 10 % surface exposure for the residue samples for different leaching potentials for Kopanang, Noligwa and Moab Khotsong ore

	Kopanang Natural Potential	Kopanang 500mV	Kopanang 700mV	Noligwa Natural Potential	Noligwa 500mV	Noligwa 700mV	Moab Natural Potential	Moab Khotsong 500mV	Moab Khotsong 700mV
Liberation	7.91	9.49	17.21	33.16	26.69	20.11	42.94	14.03	14.49
Free surface >5%	98.06	97.03	91.79	97.76	97.88	87.65	92.13	96.75	95.28
Free surface >10%	97.97	89.76	67.71	96.45	90.26	70.86	84.00	91.64	67.10

Table 6.8: Percentage uraninite liberation and percentage of brannerite with 5 and 10 % surface exposure for the residue samples for different leaching potentials for Kopanang, Noligwa and Moab Khotsong ore

	Kopanang Natural Potential	Kopanang 500mV	Kopanang 700mV	Noligwa Natural Potential	Noligwa 500mV	Noligwa 700mV	Moab Natural Potential	Moab Khotsong 500mV	Moab Khotsong 700mV
Liberation	33.53	7.37	19.30	6.14	46.05	5.32	10.38	10.12	14.01
Free surface >5%	92.44	99.10	77.65	79.69	94.12	94.22	91.07	87.80	85.47
Free surface >10%	90.46	97.56	69.33	72.62	91.10	90.86	72.96	58.39	82.62

Further, mineralogical analysis of previous tests (see Chapter 4) indicated that most of the unleached uranium exists as brannerite and it is known that the leaching kinetics of brannerite is slow [Zhang *et al.*, 2003]. Therefore, tests were carried out for 24, 48 and 72 hours to determine the effect of time on leaching. As explained in the experimental setup (see Section 6.1.2.1) fresh acid and oxidant were added after every 24 hours. To indicate that sufficient acid and potential were available throughout the tests, the end pH and Eh measurements are included in Table 6.6.

Table 6.9: Eh and pH measurements for different leaching times [1]

	24h		48h		72h	
	mV (vs. SCE)	pH	mV (vs. SCE)	pH	mV (vs. SCE)	pH
Kopanang	438.2	2.51	416.0	1.58	414.8	1.43
Noligwa	386.1	2.78	414.0	1.84	409.0	1.70
Moab Khotsong	401.7	2.41	417.0	1.60	405.9	1.63

[1] Measurements were taken at room temperature

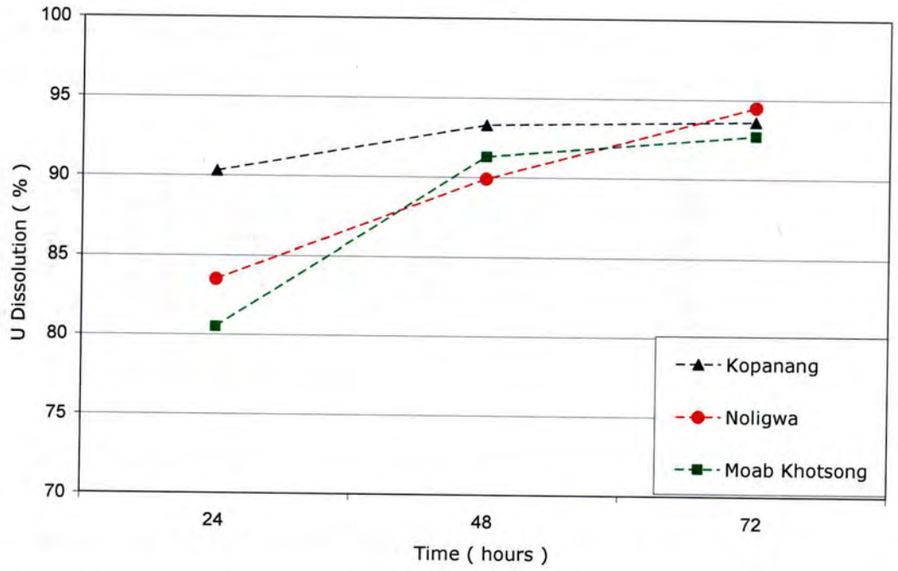

Figure 6.4: Dependency of residence time on uranium dissolution

From Figure 6.4 (as expected) an increase in residence time resulted in increasing uranium recovery. This confirms the fact that brannerite's kinetics is slow and that increasing the leaching period improve the total uranium recovery. However, the uranium leaching of Kopanang and Moab Khotsong ore flattened off after 48 hours while that of Noligwa ore was still in an upward slope. Before making any conclusions regarding the leaching characteristics of Noligwa ore it is still necessary to increase the residence time to see if it is possible to increase recovery beyond 95%. However, based on the results for Kopanang and Moab Khotsong ore it seems not possible to increase uranium recovery beyond 95 % even leaching over a 72 hour period with a over supply of acid and oxidant compare to the

amount of uranium in the ore. This confirm the results discussed after Tables 6.4 to 6.6 about the leaching of uraninite and brannerite from these ores.

Table 6.10: Uranium mineralogy (expressed as ppm) for the residue samples of Kopanang ore after tests at different leaching times

	Head Grade	Aggressive H_2SO_4 24h		Aggressive H_2SO_4 48h		Aggressive H_2SO_4 72h	
Kopanang	Start (ppm)	Left (ppm)	Dissolution (%)	Left (ppm)	Dissolution (%)	Left (ppm)	Dissolution (%)
Uranium	328.5	31.9	90.3	21.9	93.3	20.9	93.6
Uraninite	278.9	25.0	91.0	17.0	93.9	14.4	94.9
Brannerite	42.4	5.6	86.7	4.9	88.6	6.6	84.5
U_Phosphate	0.7	0.3	54.8	0.0	100.0	0.0	100.0
Coffinite	6.6	0.9	85.7	0.0	100.0	0.0	100.0

Table 6.11: Uranium mineralogy (expressed as ppm) for the residue samples of Noligwa ore after tests at different leaching times

	Head Grade	Aggressive H_2SO_4 24h		Aggressive H_2SO_4 48h		Aggressive H_2SO_4 72h	
Noligwa	Start (ppm)	Left (ppm)	Dissolution (%)	Left (ppm)	Dissolution (%)	Left (ppm)	Dissolution (%)
Uranium	389.8	64.3	83.5	39.4	89.9	21.4	94.5
Uraninite	310.7	45.1	85.5	27.4	91.17	16.5	94.68
Brannerite	72.1	18.3	74.6	11.9	83.45	4.9	93.18
U_Phosphate	0.4	0.4	0	0.0	100	0.0	100
Coffinite	6.6	0.0	100	0.0	100	0.0	100

Table 6.12: Uranium mineralogy (expressed as ppm) for the residue samples of Kopanang ore after tests at different leaching times

	Head Grade	Aggressive H_2SO_4 24h		Aggressive H_2SO_4 48h		Aggressive H_2SO_4 72h	
Maob Khotsong	Start (ppm)	Left (ppm)	Dissolution (%)	Left (ppm)	Dissolution (%)	Left (ppm)	Dissolution (%)
Uranium	602.5	117.5	80.5	52.4	91.3	43.8	92.7
Uraninite	537.4	86.4	83.9	50.0	90.7	30.3	94.4
Brannerite	46.4	29.6	36.3	2.5	94.7	12.8	72.5
U_Phosphate	2.4	1.6	34.9	0.0	100.0	0.7	70.0
Coffinite	16.3	0.0	100.0	0.0	100.0	0.0	100.0

Interestingly it is seen that there is not much difference in uranium dissolution for Kopanang ore at various leaching times. However, it did have a major influence on the uranium dissolution for Noligwa and Moab Khotsong ore. The remaining uraninite and brannerite is mostlyexposed to the leaching environment and is either liberated or associated with quartz (SiO_2) etc. (Tables can be viewed in Appendix D).

To attempt achieving 100 % dissolution, experiments were done with nitric acid (in excess) as lixiviant at evaluated temperature (90°C). This method destroys practically most minerals except quartz. Therefore, the remaining uranium is expected to be locked in quartz and will not be leachable. The residue from the tests not using additional oxidant was used. Nitric Acid digestion improves dissolution with between 15 – 17 percentage points. End dissolution percentages are presented in Table 6.9. The mass loss during these test were ± 10%. This is the maximum attainable recovery for the different ores under extreme leaching conditions. Note that tests using HF were not performed due to technical difficulties. It is recommended to do sulphuric acid tests using NaF as an oxidant since F^- has a high affinity for uranium species in solution to form a complex with the respective anions.

Table 6.13: Uranium dissolution with excess HNO_3 at 90 °C

Ore Type	U Dissolution (%)	Potential (mV vs. SCE)	pH
Kopanang	98.0	885.1	-1.04
Noligwa	98.5	888.4	-1.23
Moab Khotsong	98.6	900.7	-1.23

The bulk mineralogy and the grain size distribution of brannerite for all tests are included in Appendix D. To put it all into perspective a summary of the results obtained in Chapters 4 and 6 are presented in Figure 6.5. For Kopanang ore the uranium seems to react differently compare to the other ores due to differences in mineralogy. Form the results it is clear that the optimum uranium dissolution of Kopanang ore is reach at a constant potential of 500 mV. For Noligwa and Moab Khotsong ore more aggressive conditions are required either increasing the residence time or increasing the potential to 700 mV. If uraninite and brannerite is not the dominating minerals then the method needs to be re-evaluated. Based on these results the following can be concluded from a plant operation perspective:

Ore Type	Leaching Technique
Kopanang	Sulphuric Acid Leaching (At least 11.2 kg/t H_2SO_4 , 60°C, 24h, 4kg/t MnO_2)
Noligwa and Moab Khotsong	If the brannerite concentration is between 0-20%- Aggressive Sulphuric acid leaching (At least 13.9 and 15.9kg/t H_2SO_4 respectively, 60°C, 24h, 4kg/t MnO_2) If brannerite concentration is >20% consider more aggressive leaching methods (i.e. pressure leaching or alternative leaching agents)

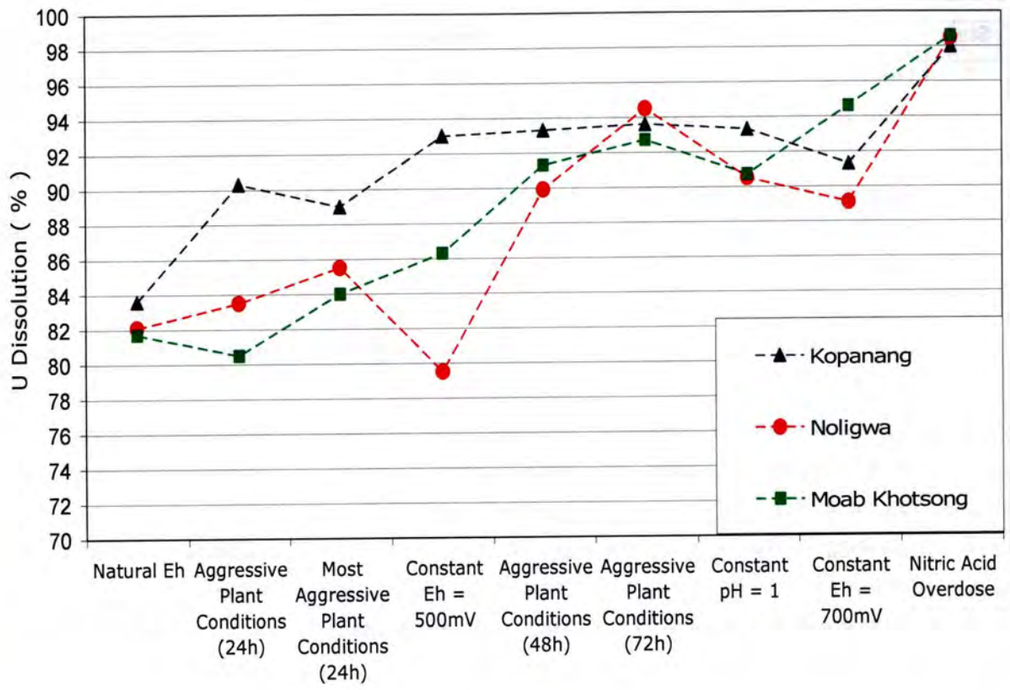

Figure 6.5: Summary of uranium dissolution results under different conditions

6.3 Step-by-step diagnostic leaching method

Table 6.14 is an easy 5 step method to be followed to fully characterise any Witwatersrand ore investigated with regards to uranium leaching.

The first step to evaluate the ore, would be to do a standard sulphuric acid leaching test without the addition of an oxidant (H_2SO_4: 16.3 kg/t; Temp: 60°C) over 24 hours to determine the amount of uranium leachable under natural potential circumstances. The residue from step 1 will then be used at aggressive conditions over 24 hours to determine the extra amount uranium leachable subjecting the ore to the maximum attainable plant conditions (H_2SO_4: 16.3 kg/t; MnO_2: 4 kg/t; Temp: 60°C) for 24 hours. The residue for step 2 must then be leached for 72 hour leaching as similar conditions to determine the effect of time on the leaching of the remaining uranium. To increase the aggressiveness of the leaching conditions step 4 involve leaching of the residue of step 3 at aggressive leaching conditions but at an evaluated temperature of 90 °C. The residue from step 4 is then leached at 700 mV for 24 hours and the unleached uranium form step 5 is then finally exposed to very aggressive leaching conditions doing nitric acid digestion also at 90 °C. The remaining uranium is uranium lock in gangue minerals (i.e. silica) and therefore not expected to leach. Based on results from these tests economical evaluations need to be done to justify process routes.

Table 6.14: Diagnostic Leaching method developed to evaluate any uranium containing ore for the Witwatersrand Basin

Step	Method	Conditions	Minerals Dissolve
1	Leaching without the addition of an oxidant for 24 hours	H_2SO_4 addition: 16.3 kg/t Temperature: 60°C	Most of the uraninite and coffinite, small amounts of brannerite, chlorite
2	Aggressive leaching conditions over 24 hours on residue of step 1	H_2SO_4 addition: 16.3 kg/t MnO_2 addition: 4 kg/t Temperature: 60°C	Remaining uraninite and coffinite, small amounts of brannerite
3	Aggressive leaching conditions over 72 hours on residue of step 2	H_2SO_4 addition: 16.3 kg/t MnO_2 addition: 4 kg/t Temperature: 60°C	Mostly brannerite, small amounts of U-Phosphates
4	Aggressive leaching conditions at 90 °C for 24 hours on residue of step 3	H_2SO_4 addition: 16.3 kg/t MnO_2 addition: 4 kg/t Temperature: 90°C	Mostly brannerite, small amounts of U-Phosphates
5	Leaching at 700 mV on the residue of step 4 for 24 hours	Eh: 700 mV Temperature: 60°C	Sulphate minerals (i.e. Pyrite)
6	Nitric acid digestion at 90 °C on the residue of step 5	HNO_3 addition: Access Temperature: 90°C	Al exposed uranium minerals left

6.4 Summary

Diagnostic leaching tests show that the uranium dissolution optimum for Kopanang ore is reached at 500 mV for 24 hours. For Noligwa and Moab Khotsong ore it is reached after 48 - 72 hours of aggressive leaching at potentials of 500 mV or at potentials of 700 mV for 24 hours. It is recommended to do sulphuric acid tests adding NaF as an oxidant since F^- has a high affinity for uranium species in solution as well as doing leaching tests at even higher constant potential as 700 mV to determine the true effect of potential on uranium mineral dissolution. Pressure leaching tests for the three ore are recommended to compare results with sulphuric acid tests. The absolute necessity for an additional oxidant need to be investigated for all three ores since the addition of an oxidant proved not to be necessary working at aggressive acid leaching concentration (16.3 kg/t) for Noligwa and Moab Khotsong ore since iron leached for ore seems to be sufficient. The lixiviant can also be evaluated, at the same time, especially with regards to the leaching kinetics of brannerite

Mineralogical analysis indicated that it is possible to leaching brannerite but, the leaching kinetics thereof is very slow. Based on the diagnostic leaching tests the following is recommended: Sulphuric acid leaching must be used for treating Kopanang ore. If the brannerite concentration of Noligwa and Moab Khotsong ore is < 20 % sulphuric acid leaching is recommended but if the brannerite concentration > 20 % other leaching methods will be recommended (i.e. pressure leaching or using a different leaching reagent).

Chapter 7

Data Analysis and Empirical Modelling

Various methods can be used to predict the expected uranium recovery for leaching a specific ore deposit, but all these methods require experimental data to a larger or lesser extend. Experiments are mostly conducted to either determine if changing the values of certain variables leads to worthwhile improvements in the mean yield of a process or to estimate the mean yield at given experimental conditions. Data analysis using statistical relations and/or pattern recognitions as the fundamental phenomenon to derive mathematical models can be used to evaluate experimental data. The advantage of this approach is that no fundamental knowledge of the process being modelled is required, but the disadvantage is that it requires a large amount of experimental data and it can only be used in the context of the experimental window tested.

Another method is empirical modelling, where the model is based on reaction rates to predict the expected uranium yield. This is a more complex method since it involves fundamental knowledge of the process, but the advantage is that fundamental problems can be addressed/solved using this method. Previous empirical modelling work done by various researchers (discussed in Section 2.7) was based on specific ores. Therefore, it can not necessary be applied directly to other ore types. The development of similar models which require mineralogical data as inputs instead including empirical values could prove beneficial. The mineralogical data can be determined on the basis of a mineralogical examination or using a diagnostic leaching method.

The aim of statistical modelling was to develop a model that is able to predict the uranium recovery (within the Vaal River context) without considering any information regarding the process. The ultimate aim is to develop an empirical model/simulator that is able to predict the recovery solely from the mineralogy of the ore (minerals themselves rather than leaching fractions). It will definitely be beneficial in the light of the fact that various ores in the Witwatersrand Basin can then be evaluated if its mineralogy is known (assuming that the reaction rates of the various minerals are the same; excluding mineral interactions). Since the development of such a model fall outside the scope of this project, this chapter will only include a proposal for such a model.

7.1 Data Analysis and Statistical Modelling

Accepted methods to model such experiments include regression analysis. Regression analysis refers to the interpretation of a finite population of data by exploring the relationship between several variables using the principle of regression. It is recommended to start with the simplest (linear model) then moving to more complex non-linear models.

7.1.1 Linear Model

Evaluation of this process involves estimation of the dependency of the recovery of uranium on the process conditions, such as temperature, acid concentration, oxidant concentration, time as well as the mineralogy (ore type). For a first approach a linear model was used to predict the total uranium dissolution as a function of the various parameters. The following model [7.1] was formulated combining the data of the 3 different ores (using Excel®):

$$\mathbf{Y} = 30.61 - 0.46\ (\mathbf{ORE\ TYPE}) + 2.01\ (\mathbf{TIME}) + 0.50\ (\mathbf{ACID}) - 0.002\ (\mathbf{OXIDANT}) + 0.02\ (\mathbf{TEMPERATURE}) \quad [7.1]$$

Y is the total expected uranium in dissolution; **ORE TYPE**: Kopanang=1; Noligwa=2; Moab Khotsong=3, **TIME** is in hours; **ACID** is in kg/t as well as **OXIDANT** and **TEMPERATURE** is in °C.

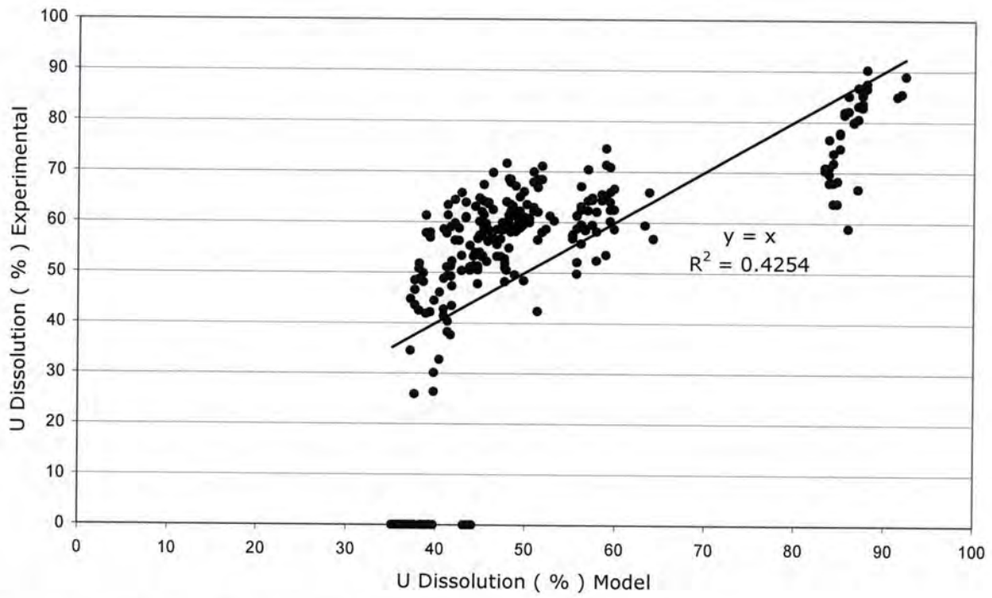

Figure 7.1: Evaluation of the linear model for the uranium leaching process

The regression statistics indicate that a linear model is not an effective approach to model the data (Figure 7.1 and Table 7.1). An R^2 value of less that 0.5 indicates that the model accounted for less than 50 % of the variation in the data. Evaluating the coefficients of the model did not necessarily give information regarding the process since the data was not standardised initially. It is recommended that the data be standardised before fitting a linear model, but since the data do not seem to have linear properties a non-linear model was rather considered.

Table 7.1: Regression statistics of the linear model

Regression Statistics	
Multiple R	0.65222
R Square	0.42539
Adjusted R Square	0.41434
Standard Error	18.16143
Observations	266

7.1.2 Non – Linear Model

There are various non-linear techniques available, but the nature of the data forms some guidelines to which method will best describe the process. In the case that the relationship between the response and the predictor is not known a more nonparametric type of regression fitting approach can be followed. One such approach is based on decision trees. It is equivalent to a set of IF-THEN rules, which can be incorporated into a knowledge-based decision support system and predictors can be either continuous or discrete. Decision trees are one of the most widely used methods for modelling and interpretation of data since the methodology is well known. It provides a simpler and more intuitive interpretation of datasets and do not necessitate use of expect programs to implement the method. This method can also be used manually (to interpret results) which will definitely be beneficial in a plant operation context. Although decision trees were originally designed for large datasets it has also proven to be valuable for the analysis of smaller datasets. (For further reading regarding classification trees refer to Breiman *et al.*, 2003)

Many approaches can be followed which will strongly depend on the expected outcome to be achieved. The initial idea behind the development of such a model is not necessarily to be able to predict the expected recovery in terms of operating condition but rather to get more information regarding the process (i.e. to be able to determine the operating condition necessary to achieve recovery in a specific range). Therefore, the problem was treated as a classification problem rather than a regression problem. A classification tree is a sequence of questions that can be answered as yes or no that can be used to classify the data. Each question asks whether a predictor satisfies a given condition. If the condition is satisfied keep left else go right and proceed to another question or arrive at a fitted response value. A model was developed using Matlab®. For analysis of the data the data set was divided into 3 sets. Three different trees were developed each time using 2 thirds of the data for training and one third for testing. The data were divided into three different classes and the

ranges for % uranium recovery were specified as follow: Class 1: 0-50%; Class 2: 51-70% and Class 3: 71-100%. These ranges can be adjusted for plant operation purposes. The input variables are standardised beforehand to incorporate the true effect. The developed model is presented in Figure 7.2 and can be interpreted as follow: Variables at the top of the three are generally most influential in terms of maximising homogeneity and as seen in Figure 7.2 it can be noted that time (as expected) is the most influential parameter. Take note that Ore 1, Ore 2 and Ore 3 refer to Kopanang, Noligwa and Moab Khotsong respectively. Further investigating the branches of the tree it is clear that in terms of plant operation variables acid is most crucial as also pointed out in Chapter 4 - Section 4.2.1.

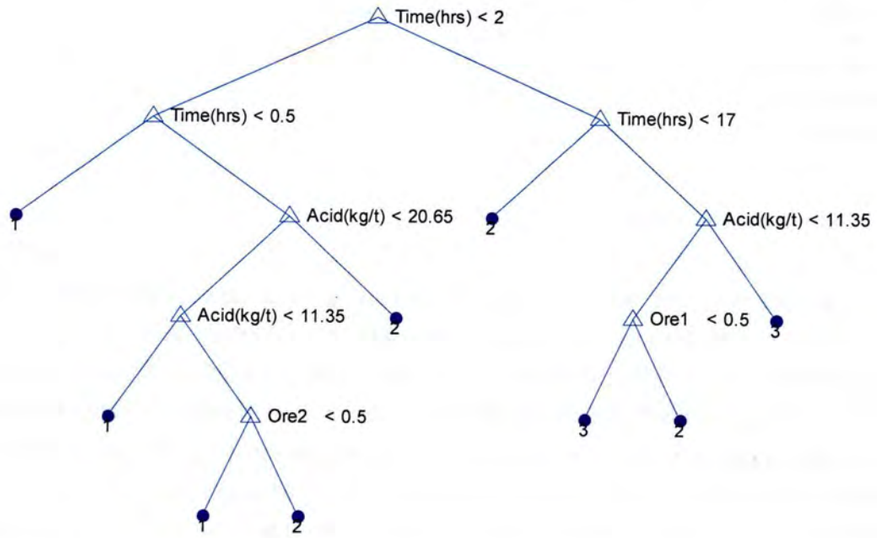

Figure 7.2: Classification tree for analysis of the experimental data of the three different ores

With noisy data the algorithm will build a decision tree that is consistent with all the data in the training set but will most likely lead to over fitting. Some of its lower branches might be strongly affected by outliers of the current data set. Therefore, it is recommended to develop a simpler tree that avoids this problem of over fitting. It is possible to estimate the best tree size by cross validation. Firstly, a resubstitution estimate of the error variance for this tree is computed as well as a sequence of simpler trees, which is plotted as the lower (blue) line in Figure 7.3. This estimate probably under-estimates the true error variance. A cross-validation estimate of the same quantity is then computed and plotted as the upper (red) line. The cross-validation procedure also provides an estimate of the pruning level needed to achieve the best tree size. The best tree is the one that has a residual variance that is no more than one standard error above the minimum value along the cross-validation line. In this case the variance is 3. Furthermore, this output is used to create a smaller tree that is pruned to the estimated best size. From the pruned tree only considering 3 nodes are considered.

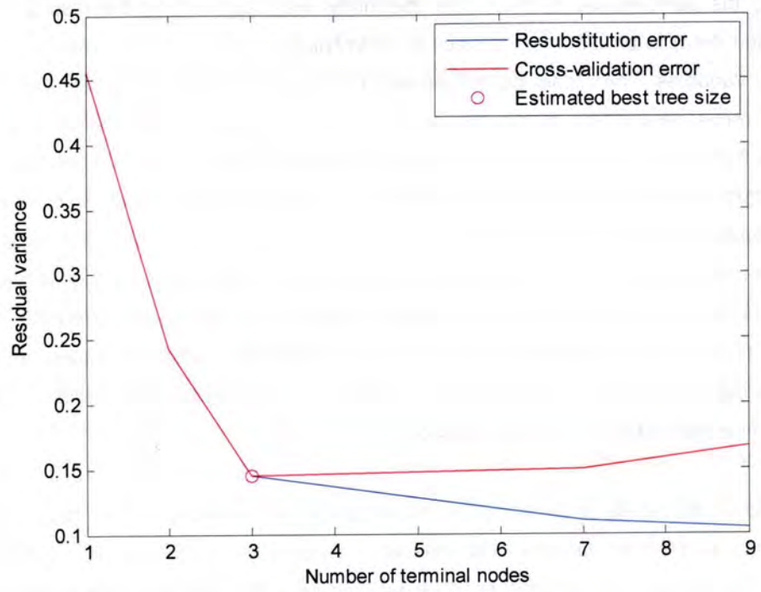

Figure 7.3: Cross validation to determine the best tree size

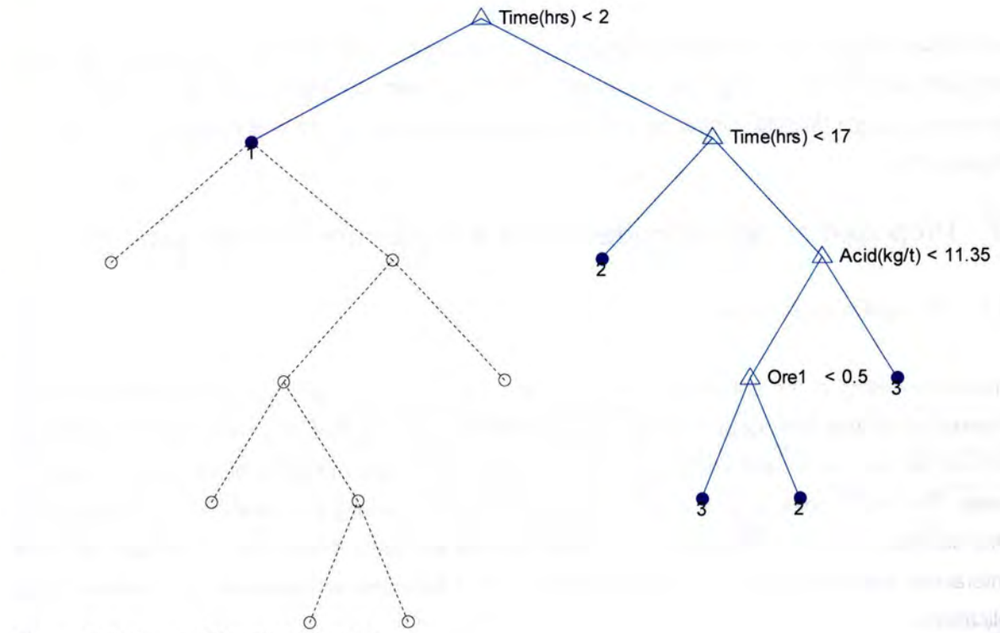

Figure 7.4: Pruned classification tree

The pruned tree indicates that in order to achieve dissolutions higher than 70 % a leaching time longer than 17 hours are required as well as an acid addition concentration higher than 11.35 kg/t for Noligwa and Moab Khotsong but lower acid concentration can be tolerated for Kopanang ore. This corresponds to the experimental findings as discussed in Chapter 4.

Investigating the performance of the model, the model was tested using the testing data (that is not pre-processed data) to predict the accuracy of classifying the data into the respective classes based on the input variables. The model performed well being able to classify the data with 86% accuracy. To test the robustness of the model this method was repeated 3 times using randomised data to develop the tree. Using this method it is possible to classify the data with a mean accuracy of 84 % and a standard deviation of 2.8 % implying that it is a representative model. Since the use of such a model will mainly focus on a specific range (range 3) it is necessary to further investigate the accuracy of prediction in that specific range. The ideal is that the amount of samples is evenly distributed across all three classes but only 36 of the 266 samples were part of class 3. Nevertheless the model was able to correctly predict with an average accuracy of 74 % for the 3 different models developed with a standard deviation of about 15 %. To improve the accuracy more data points in class 3 will be required, hence more experiments are required.

To determine the sensitivity of the model to the variables the modelling procedure was repeated, each time removing a different variable. The operating parameters were the only variables that were considered. The various models were then validated to determine the influence of the specific variable on the accuracy of the prediction. No specific trends could be found but based on the layout of the tree (Figure 7.2) it can be assumed that acid is the most crucial operating parameter.

As previously mention this statistical model is not developed to predict an exact recovery but more realistically predicting a range for expected recovery based on the operating conditions. The developed program (Matlab® Code) as well as instructions to use the model is included in Appendix E – Section 14.1.

7.2 Proposed empirical modelling for the uranium leaching process

7.2.1 Program Description

Empirical modelling of the uranium leaching process was not part of the original scope of the project, but based on all the information gathered throughout the study the following model can be proposed which can be used as a base line for any further studies concerning modelling of the uranium leaching process. Previous modelling work done by Phala [2005] on Kopanang ore were used as starting point for the development of the proposed model. Note that this proposed model does not include the effect of interaction between various minerals and need to be taken into consideration for future modelling applications.

Evaluation of the mineralogy of the Vaal River ores indicates the following: (i) Uranium grain sizes were found to be very small, with 50 % of the particles passing 19.4, 21.3 and 23.2 µm for Kopanang, Noligwa and Moab Khotsong respectively; (ii) the degree of liberation of the main uranium-bearing minerals was low (see Table 3.9 and Table 3.10), between 11 and 45 %, and expectedly increased as particle size decreased. In case of poor liberation the uranium particles can not be considered as

isolated and therefore the leaching process would be best described through something like a shrinking core model. However, it is important to realise that minerals do not necessarily leach according to a shrinking core model, but will rather leach along grain boundaries. Further investigation of the mineralogy indicated that the uranium minerals have high surface area exposure (Table 3.9 and Table 3.10) despite low liberations. Therefore, the system can be simplified since it will be exposed to the leaching environment, thus eliminating the diffusion factor assuming that the ore particles are fully suspended.

Reactions between more than one phase (i.e. between the liquid and solid phase) usually occurs at or very close to the interface between the phases. In the 1980's Eary and Cathless [1983] proposed a three step mechanism for the dissolution in H_2O_2 media at acidic pH (from 1.2 to 5.5). Factors to consider are: (1) adsorption of H_2O_2 on to the UO_2 surface; (2) oxidation of U^{4+} to U^{6+} via a electrochemical mechanism; and (3) the desorption of the species. For a first approach step (2) will be assumed as being the limiting step. Mathematically the elementary rate law can be expressed as follows [Fogler,1999]:

$$-r_A = -\frac{\partial C_A}{\partial t} = k_A (C_A)^{\alpha} (C_B)^{\beta} \qquad [7.2]$$

In equation [7.2] k_A (specific rate of reaction) is not a true constant and is highly dependent on temperature. It is also a function of total pressure, but the effect of pressure is negligible compared to the effect of temperature. A reaction occurs when molecules collide with sufficient energy (called activation energy) to break the bonds. The rate constant and activation energy is related by the Arrhenius equation [7.3] [Fogler, 1999] with A the pre-exponential factor / frequency factor, E the activation energy (J/mol), R the gas constant (8.314 J/mol.K) and T the absolute temperature (K):

$$k_A (T) = A.e^{E/R.T} \qquad [7.3]$$

Empirical modelling of a specific ore body (Witwatersrand Basin) will require deriving rate constants using experimental data. Since uranium leaching is proved to be of electrochemical nature [Nicol *et al,* 1979], it is necessary to include the Butler-Volmer equation [7.4] to incorporate the current flow (reaction rate with the electrode potential at the electrode/electrolyte interface) [Hayes, 2003]:

$$j = j_o \left\{ \exp\left(\frac{-n\beta F\eta}{RT} \right) - \exp\left(\frac{n(1-\beta)F\eta}{RT} \right) \right\} \qquad [7.4]$$

In equation [7.4] j represents the current density across the electrode/electrolyte interface (Am^{-2}), j_o the exchange current density (Am^{-2}), β is a constant dependent on the electrolyte and the electrode and η is the over potential on the electrode (V).

For the development of this model, only relevant minerals (with reference to uranium dissolution/reagent consumption) will be considered. Based on the evaluation of the residue samples of the leaching experiments the following minerals will be considered for modelling: UO_2 (uraninite), $UO_2.2TiO_2$ (brannerite), MnO_2 (manganese dioxide), FeO (iron oxide), FeS_2 (pyrite) and $Mg_2Fe_2Al_{3.3}Si_{2.5}O_{10}(OH)_8$ (chlorite).

Schematic model of the uranium leaching process:

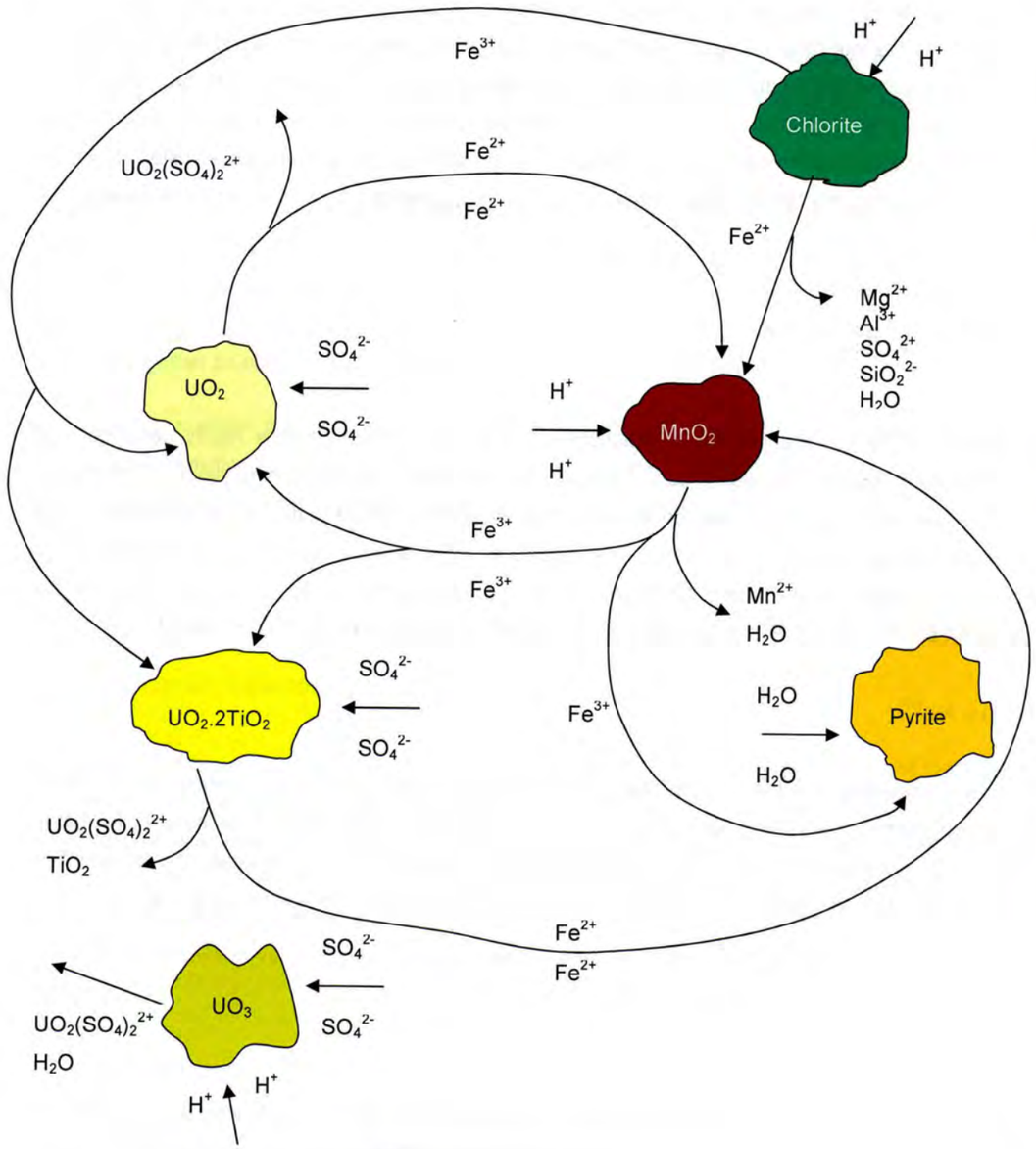

Figure 7.5: Schematic diagram of the uranium leaching process

Uraninite Leaching:

Due to its electrochemical nature, uraninite (UO_2) will leach according to the following oxidation/reduction reactions:

$$UO_2 \leftrightarrow UO_2^{2+} + 2e^- \quad [7.5]$$

$$2Fe^{3+} + 2e^- \leftrightarrow 2Fe^{2+} \quad [7.6]$$

Stable sulphate-complexes from during acid leaching of UO_2 due to the presence of sulphate ions and the de-ionation of sulphuric acid [Merritt, 1971]:

$$UO_2^{2+} + SO_4^{2+} \leftrightarrow UO_2SO_4 \quad [7.7]$$

$$UO_2SO_4 + SO_4^{2-} \leftrightarrow [UO_2(SO_4)_2]^{2-} \quad [7.8]$$

$$[UO_2(SO_4)_2]^{2-} + SO_4^{2-} \leftrightarrow [UO_2(SO_4)_3]^{4-} \quad [7.9]$$

According to Burneau *et al.* [1992] the equilibrium constants (in terms of activity) for reactions [7.7] and [7.8] are 1400 and 11 respectively, while for reaction [7.9] it has no significant value. Therefore it is safe to assume that reaction [7.9] is negligible. The positive values of k indicate that the products are favoured over reactants at equilibrium ($-\Delta G$: Reaction proceeds spontaneous at all temperatures). Including reactions [7.7] and [7.8], the oxidation reaction for uraninite can be described as follow:

$$UO_2 + 2SO_4^{2-} \leftrightarrow UO_2(SO_4)_2^{2-} + 2e^- \quad [7.10]$$

The standard potential for the uranium oxidation reaction must be revised since it needs to correspond to reaction [7.10]. One way to approach this is to consider the three reactions separately as shown in reaction [7.11]. Complexation of the naked UO_2^{2+} ion by SO_4^{2-} is a favourable process and indeed lowers the required potential to oxidise uraninite (as shown by the calculation). This point has been largely ignored, since in previous work the standard potential (E^0) for UO_2^{2+} is used and not $[UO_2(SO_4)_2]^{2-}$, which is more applicable. With this approach it will also be possible to explain behaviour of different ligands (e.g. F, Cl, Br, etc) when their k values are known.

$$E^o_{Uraninite} = E^o_{UO_2/UO_2^{2+}} + E^o_{UO_2^{2+}/UO_2SO_2} + E^o_{UO_2SO_2/UO_2(SO_2)_2^{2-}} \quad [7.11]$$

$$= \frac{\Delta G_{UO_2/UO_2^{2+}} + \Delta G_{UO_2^{2+}/UO_2SO_2} \Delta G_{UO_2SO_2/UO_2(SO_2)_2^{2-}}}{-vF}$$

$$= \frac{(75270 - 17957.1 - 5943.95)\,J/mol}{-(2)(96500\,J/V.mol)}$$

$$= -0.27V$$

The reaction rate:

$$-r_{UO_2} = k_{UO_2}\ e^{\frac{(1-\beta)F\left(E_m - E^o{}_{UO_2}\right)}{RT}}\ [UO_2]\ \left[SO_4^{2-}\right]^2 \qquad [7.12]$$

Including the reduction reaction [7.6] the reaction rate of UO_2^{2+} simplifies to:

$$r_{Fe^{3+}} = -k_{Fe^{3+}}\left[e^{\frac{-\beta F\left(E_m - E^o_{Fe}\right)}{RT}}\right]\left[Fe^{3+}\right] + k_{Fe^{2+}}\left[e^{\frac{(1-\beta)F\left(E_m - E^o_{Fe}\right)}{RT}}\right]\left[Fe^{2+}\right] \qquad [7.13]$$

$$\therefore r_{UO_2} = 2\left|r_{Fe^{3+}}\right| \qquad [7.14]$$

$$E^o{}_{Ee^{3+}} = 0.77V \quad (vs.\ SHE)$$

Making E_m the subject of the equation and assuming a tafel constant (β) of 0.5 [Nicol et al., 1979]:

$$E_m = \left[\frac{RT}{-F}\ln\left[\frac{k_{UO_2}e^{\frac{-0.5FE^o{}_{UO_2} + 0.5FE^o{}_{Fe}}{RT}}[UO_2][SO_4{}^{2-}]^2 - 2k_{Fe^{2+}}[Fe^{2+}]}{-2k_{Fe^{3+}}[Fe^{3+}]}\right]\right] + E^o{}_{Fe} \qquad [7.15]$$

Only considering UO_2 it was found that it is impossible to explain the ± 60 % of uranium that dissolve with in the first few hours. Based on that is necessary to incorporate the fact that uraninite may exist as a mixture between UO_2 and UO_3. Tetravalent uranium has a low solubility in acid while hexavalent uranium is readily soluble in acid media. This coincide with previous modelling work done by Ford and Gould [1994], Macnaughton *et al.* [1999] and Phala [2005] taking into account that different uranium minerals react differently. They created a four term uranium leaching model dividing uranium minerals into four categories: (i) fast, (ii) medium, (iii) slow and (iv) non leaching (fraction not accessible to leaching). In the modelling context UO_3 an UO_2 will correspond to the fast and medium leaching fraction. It was found, during the modelling exercise, that a UO_3:UO_2 ratio of 80:20 best described the dissolution-time leaching profile.

$$UO_3 + 2H^+ \leftrightarrow UO_2^{2+} + H_2O \qquad [7.16]$$

The rate equation describing equation [7.16]:

$$-r_{UO_3} = k_{UO_3}[UO_3][H^+]^2 \qquad [7.17]$$

Brannerite Leaching:

Zhang *et al.* [2003] studied synthetic brannerite samples and found that under acidic environments, uranium release from brannerite is incongruent, meaning that UO_2 is released while TiO_2 is left behind therefore the proposed oxidising reaction form brannerite leaching is as follows:

$$UO_2.2TiO_2 + 2SO_4^{2-} \leftrightarrow UO_2(SO_4)_2^{2-} + 2TiO_2 + 2\ e^- \qquad [7.18]$$

From the free energies of formation of UO_2 and UO_2^{2+} [Ulmann's Encyclopaedia, 1996; U.S.N.B.S. Tables, 1982], it was calculated that a potential of 0.39 V (vs SHE) is required to oxidise pure uraninite to UO_2^{2+}. The enthalpy for the reaction of synthetic brannerite (Uti_2O_6) to UO_2 and TiO_2 is 7.7±2.8 kJ/mol [Helean *et al.*, 2003]. If the free energy is assumed to be approximately equal to this reaction enthalpy (the entropy is not known), then the thermodynamic cycle shown in equation [7.19] can be used to estimate the potential required to leach brannerite (incongruently):

$$E^o{}_{Brannerite/UO_2} \approx \frac{\Delta H}{-vF} \qquad [7.19]$$

Therefore:

$$\begin{aligned} E^o{}_{Brannerite/UO_2(SO_4)_2^{2-}} &= E^o{}_{Brannerite/UO_2} + E^o{}_{UO_2/UO_2^{2+}} + E^o{}_{UO_2^{2+}/UO_2SO_4} + E^o{}_{UO_2(SO_4)_2^{2-}} \\ &\approx \frac{\Delta H_{Brannerite/UO_2} + \Delta G_{UO_2/UO_2^{2+}} + \Delta G_{UO_2^{2+}/UO_2SO_4} + \Delta G_{UO_2(SO_4)_2^{2-}}}{-vF} \\ &\approx \frac{(7700 + 75270 - 17957.1 - 5943.95)^J/_{mol}}{-(2)\left(96500^J/_{mol}\right)} \\ &\approx -0.30606V \end{aligned} \qquad [7.20]$$

By using equation it is not necessarily implying that the brannerite forming UO_2 and $2TIO_2$ is electrochemical, the values are just normalised so that it is all given per electron. This is simply a thermodynamic cycle. Brannerite leaching corresponds to the slow leaching fraction in terms of conventional uranium modelling terminology. The reaction rate for the formation of $UO_2(SO_4)_2^{2-}$ from brannerite is presented in equation [7.21]

$$r_{UO_2(SO_4)_2^{2-}} = k_{UO_2 2TiO_2}\ e^{\frac{(1-\beta)F\left(E_m - E^o{}_{UO_2 2TiO_2}\right)}{RT}}\ [UO_2 2TiO_2]\ \left[SO_4^{2-}\right]^2 \qquad [7.21]$$

The mix potential of the system is assumed to be equal to reaction [4.14]. Since only the activation energy of UO_2 is known, the rate constants are not included in terms of activation energies.

Chlorite Leaching:

$$Mg_2Fe_2Al_{3.3}Si_{2.5}O_{10}(OH)_8 + 4H_2SO_4 \leftrightarrow 2Mg^{2+} + 1.7Fe^{2+} + 0.3Fe^{3+} + 3.3Al^{3+} + 4SO_4^{2-} + 2.5SiO_4^{2-} + 8H_2O \quad [7.22]$$

$$r_{Chlorite} = k_{Chlorite}[H^+][Chlorite] \quad [7.23]$$

Pyrite Leaching:

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad [7.24]$$

$$r_{Pyrite} = k_{Pyrite}[Fe^{3+}][Pyrite] \quad [7.25]$$

Manganese Dioxide Leaching:

$$MnO_2 + 4H^+ + 2Fe^{2+} = Mn^{2+} + 2H_2O + 2Fe^{3+} \quad [7.26]$$

$$r_{MnO_2} = k_{MnO_2}[Fe^{2+}][MnO_2] \quad [7.27]$$

Potential:

The applied potential to the system can be determined theoretically by the following expression:

$$E_h = 0.771 + \frac{RT}{nF}\ln\left[\frac{aFe^{3+}}{aFe^{2+}}\right] \text{ (V)} \quad [7.28]$$

Due to no knowledge of the activity coefficients of both the ferric and ferrous ions it is decided rather to determine the potential equation experimentally. Experimental data was used to derive an expression to fix redox measurements taken with reference to a standard calomel electrode. Converting it to SHE the following expression was developed: (SHE = SCE+243mV)

$$E_h = 0.683 + 7.4x10^{-5}T\ln\left[\frac{Fe^{3+}}{Fe^{2+}}\right] \text{ (V)} \quad [7.29]$$

Note that the redox was measured at room temperature and not reaction temperature.

pH:

This model is setup for sulphuric acid leaching. When calculating the pH value it is important not to assume a unity activity factor when determining the correlation between sulphuric acid and the actual pH since the activity factor influences the pH [Chang, 1998] see equation [4.30].

$$pH = -\log(\gamma\,[H^+]) \quad [7.30]$$

Using experimental data an activity factor of 0.87 was calculated using Excel® solver.

The methodology was coded in Python®. The rate constants for the different reaction can be determined either experimentally or numerically by sum of square minimisation. To make fully use of this program (it can be use for uranium dissolution prediction, uranium dissolution optimisation as well as explaining the leaching kinetics) it is necessary to determine the k-values. It is programmed in Python® such that the leaching results are exported to Excel which can then further be used. The Python® code is included in Appendix E. It can be used for the three different ores as well as other ores. At "Select ore type:" choose 4 or evaluating a new ore type and enter the mineralogy as specified.

7.2.2 Process Simulation

Random k-values were used just to explain the trends that were obtained experimentally (k-values will only influence absolute values but not the overall trends). A typical example is included and Figure 7.6 – Figure 7.9 represent results obtained. In Figure 7.7 it can be seen that the pH increase during the process as expected (due to acid consumption) and the Eh drastically increase after the addition of an oxidant and then gradually decrease. The reagent profiles also agree with experimental results. Acid concentration drastically decrease, Fe^{2+} and Fe^{3+} form in the first 1.5 hours (chlorite dissolution) before the addition of MnO_2 and thereafter the Fe^{3+} increase due to the regeneration of Fe^{2+} to Fe^{3+}. The MnO_2 concentration is 0 until the addition of oxidant (after 1.5 hours) and then gradually decreases (see Figure 7.8). The most important is the uranium leaching profiles and to prove that using the UO_3, uraninite and brannerite leaching rates it is possible to explain the leaching profiles. It is expected that UO_3 will leach very quickly, uraninite dissolution will increase after the addition of the oxidant and brannerite leaching rate will be very slow (due to slow leaching kinetics) as can be seen in Figure 7.9.

```
In [6]: run UModelML3Sept2007.py
##############################################################################
      URANIUM ACID LEACHING MODEL PREDICTOR OF WITWATERSRAND ORE
##############################################################################
Select Ore type:
1          Noligwa
2          Kopanang
3          Moab Khotsong
4          Other
0          Exit
>> 2
Mineralogy chosen:  Kopanang
Enter mass % solids:56
Enter Uranium Head Grade in kg U3O8/t):0.03
Enter Pyrolusite addition in kg/t:4
Enter H2SO4 addition in kg/t:25
Enter Leaching Temperature in deg C:60
Enter Leaching Time in hours:24
Close figures to continue
Press enter to close graphs
Time conversion data can be viewed in file leachmodel.xls
```

Figure 7.6: Description of the process evaluated as run in Python®

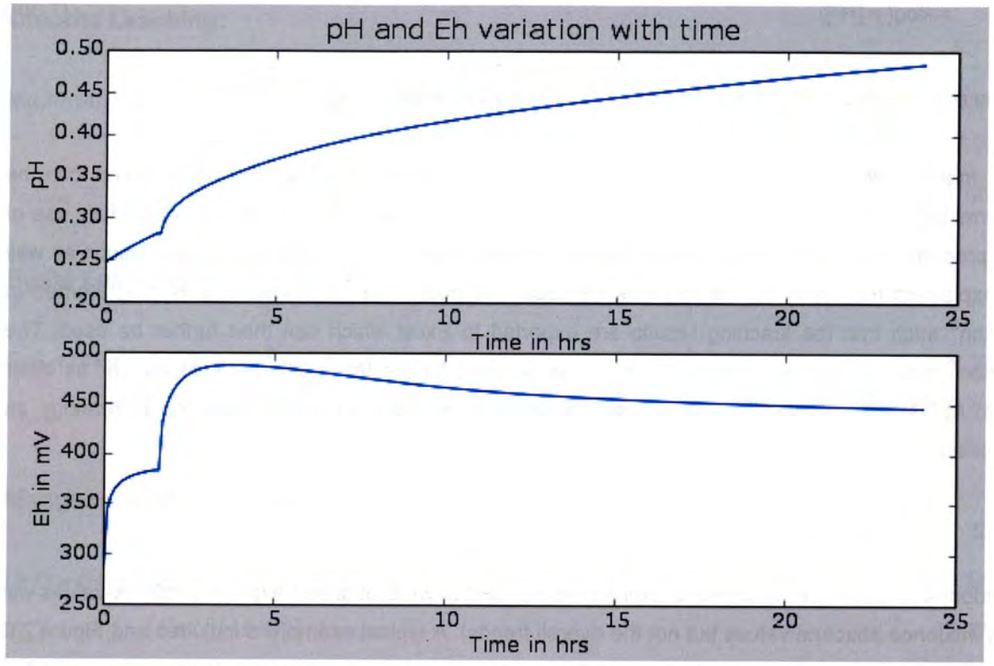

Figure 7.7: Eh and pH profile of the simulated process

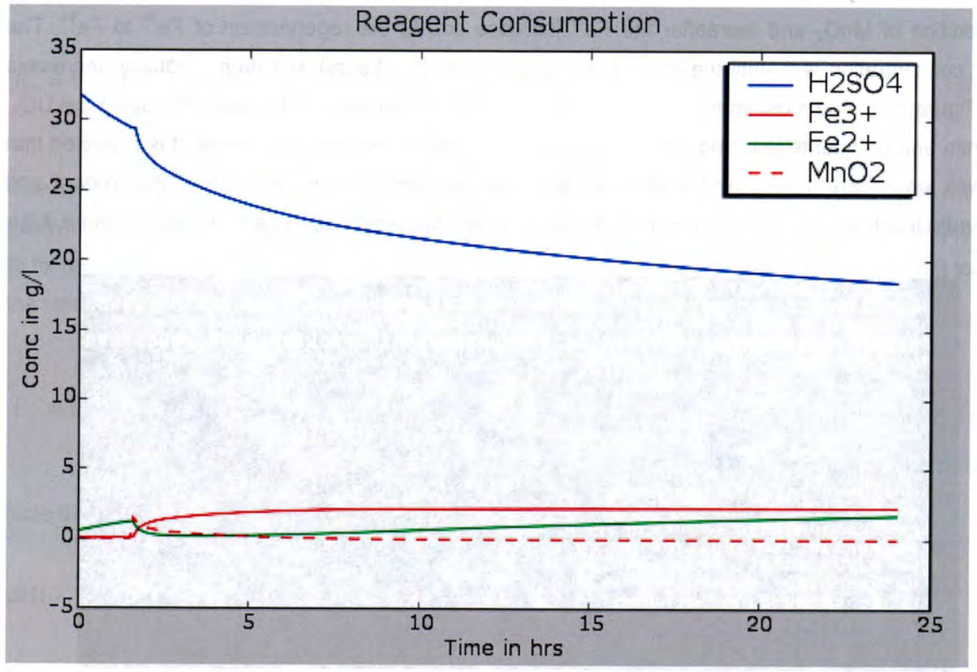

Figure 7.8: Reagent profiles for the simulated process

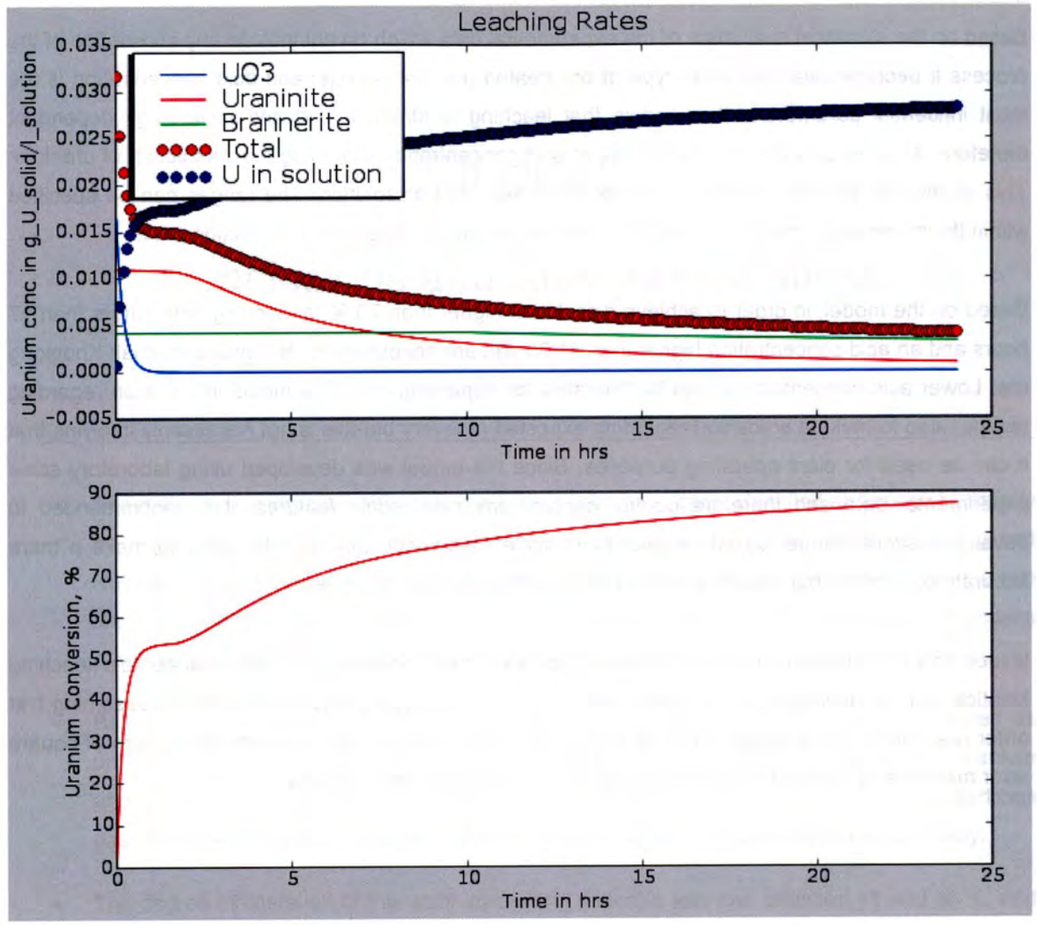

Figure 7.9: Leaching rates of the different uranium minerals as well uranium conversion graph for the simulated process

7.3 Summary

The developed model was tested using data that is not pre-processed and was able to classify the data into the respective classes with 86% accuracy based on the input variables. To test the robustness of the model three different decision trees were developed each time using random data. Using the three different trees it was possible to classify the data with a mean accuracy of 84 % and a standard deviation of 2.8 % implying that it is a representative modelling method. The targeted range is class 3 and only proved to accurately classify the data in that class with an average accuracy of 74 % and standard deviation of 15 % for the 3 different tree models developed. It is recommended that in order to improve the accuracy more data points in class 3 will be required hence more experiments are required.

Based on the statistical evaluation of the experimental data which do not include any knowledge of the process it become clear that time, type of ore treated (i.e. mineralogy) and acid concentration is the most influential parameters. It is known that leaching is strongly time and mineralogy dependant therefore, it just emphasise the importance of acid concentration regarding the dissolution of uranium. This model can be used to predict the range of expected dissolution. The ranges can be specified within the model. Instructions to use the model are included in Appendix E – Section 14.1.

Based on the model, in order to achieve dissolution higher than 70 %, a leaching time longer than 17 hours and an acid concentration higher than 11.35 kg/t are necessary for Noligwa and Moab Khotsong ore. Lower acid concentrations can be tolerated for Kopanang ore. This model information regarding can be used to make a prediction regarding expected recovery but this is not necessarily implying that it can be used for plant operating purposes. Since the model was developed using laboratory scale experimental data and therefore do not capture any plant scale features. It is recommended to develop a similar model based on pilot plant scale data which than can be used to make a more accurate predictions but moreover can be used to optimisation purposes.

Issues to be addressed in future research include further investigation into brannerite's leaching kinetics and the development of rate expressions for the various gangue minerals (not assuming first order reactions). The k-values must be determined experimentally or calculated doing sum of square error minimisation instead of guessing k-values to fit the experimental data.

Chapter 8

Conclusions and Recommendations

- The major bulk minerals in the three Vaal River ores have been identified and consist primarily of quartz (70 – 80 %), with lesser amounts of muscovite (8 – 11 %). Moab Khotsong and Noligwa ore samples were found to be very similar, and Kopanang is different from the two ores. Kopanang ore has less pyrite, quartz, and chlorite than the other two ores, but contains more pyrophyllite (9.7 %), as compared to the other ores.

- Bulk uranium analysis showed that 80 – 90 % of the uranium in the ores is contained as uraninite, 8 – 19 % as brannerite, and the balance as traces of coffinite and uranium phosphates. Uranium grain sizes were found to be very small, with 50 % of the particles passing 19.4, 21.3 and 23.2 µm for Kopanang, Noligwa and Moab Khotsong respectively.

- The degree of liberation of the uranium-bearing minerals was low, between 11 and 45 %, and expectedly increased as particle size decreased. No relationship between surface area exposure and liberation existed when liberation was poor. Uranium minerals seem to have high percentage surface exposure despite poor liberation. This indicated that coarser grinds can be tolerated for uranium leaching.

- It was found that it is very difficult to achieve uranium dissolutions higher than 90 % for the Vaal River ores under conventional uranium leaching conditions. The predominant uranium mineral in the leach residue samples is brannerite. Although insufficient surface area was initially suspected to be the limiting factor, the proportion of brannerite mineral in the leach residue that has more than 10 % of the particle surface exposed (thus being accessible to the leach solution) between ~ 58 % and 92%, similar to that in feed samples. A significant quantity of brannerite in the residue samples is also fully liberated. This shows that brannerite is intrinsically slow leaching, and association with gangue minerals is not the main cause of the slow kinetics.

- The residue mineralogies of the three ores are very close. Under realistic operating conditions for Vaal River, the following uranium dissolutions can be assumed: Kopanang: 85 – 90 %;

Great Noligwa: 80 – 85 %; Moab Khotsong: 80 – 85 %. These dissolutions are obtainable within a 24 hour leaching period. Pyrolusite addition must be based on the soluble iron produced by the reactions of Fe-bearing gangue (e.g. chlorite) with acid. Kopanang ore requires at least 11 kg/t acid, while acid requirements for Great Noligwa and Moab Khotsong ores are 14 and 16 kg/t respectively, at a leaching temperature of 60°C.

- Aggressive leaching conditions (as defined in this thesis) are thought to be suitable for extracting maximum value out of an atmospheric leach set-up. If ~ 100 % extraction is desired, more extreme conditions (probably pressure leaching) will be necessary.

- In Vaal River, uranium production is only economical in conjunction with gold production. Therefore, the benefits of a reverse-leach operation were investigated. It was found that a gold benefit of 0.4 - 0.6 g/t can be realised by extracting uranium before gold. Therefore, reverse leaching of gold is a financially justified practice.

- Diagnostic leaching results indicated that to improve uranium dissolution beyond 90 % uneconomical conditions (residence time between 48 and 72 hours, constant pH = 1 or Eh = 700 mV) need to be considered and it will still not be possible to increase beyond 95%. The maximum obtain is 98% during nitric acid digestion at evaluated temperature (90°C).

- A uranium diagnostic method for the evaluation of any Witwatersrand ore include the follow 4 step (this method is developed of ore containing mainly uraninite and brannerite):

  Step 1: Aggressive acid leaching without addition of additional oxidant over 24 hours
  Step 2: Aggressive acid leaching over 24 hours on residue of step 1
  Step 3: Aggressive acid leaching over 72 hours on residue of step 2
  Step 4: Aggressive acid leaching over 24 hours at 90 °C on residue of step 3
  Step 5: Leaching at 700 mV at 60°C over 24 hours on residue of step 4
  Step 6: Nitric acid digestion on the residue of step 5 at 90 °C

- It will also be recommended to do sulphuric acid tests adding NaF as an oxidant since F^- has a high affinity for uranium species in solution as well as doing leaching tests at even higher constant potential as 700 mV to determine the true effect of potential on uranium mineral dissolution.

- The addition of an oxidant proved not to be necessary working at aggressive acid leaching concentration (16.3 kg/t) for Noligwa and Moab Khotsong ore since iron leached for ore seems to be sufficient. The absolute necessity for an additional oxidant need to be investigated for all three ores.

- Mineralogical analysis indication that it is possible to leaching brannerite but that the leaching kinetics thereof is very slow.

- Based on the diagnostic leaching tests the following is recommended: Sulphuric acid leaching must be used for treating Kopanang ore. If the brannerite concentration of Noligwa and Moab Khotsong ore is < 20 % sulphuric acid leaching is recommended but if the brannerite concentration > 20 % other leaching methods is recommended (i.e. pressure leaching or using a different leaching agent).

- It is recommend to do pressure leaching on the three different ore and to compare to results obtain for sulphuric acid leaching tests.

- A statistical model was developed to evaluate experimental data. Decision tree analysis was found to best describe the characteristics of the data. It was decided to rather consider the problem as a classification problem as compared to regression. It is more realistic to rather predict a range for expected dissolution rather than trying to predict the absolute amount. The model proved to be representative accurately classifying experimental data with a mean average of 84 % and standard deviation of 2.8 %.

- The model only proved to accurately classify the data in the higher range (i.e. class 3) with an average accuracy of 74 % and standard deviation of 15 % for the 3 different tree models developed. It is recommended that in order to improve the accuracy more data points in class 3 will be required hence more experiments are required.

- The model is not very complex and indicates that in order to achieve dissolution higher than 70 % a leaching time longer than 17 hours and an acid concentration higher than 11.35 kg/t are necessary for Noligwa and Moab Khotsong ore while lower acid concentrations can be tolerated for Kopanang ore.

- The development model (decision tree model) can be used to make predictions regarding the expected dissolution range within the Vaal River context but can not be used for plant operation / optimisation purposes since the model do not capture plant scale features. Therefore, it is recommended to develop a similar model using pilot plant scale data.

- From experimental data it was found that ± 60 % of uranium dissolve readily, before the addition of pyrolusite. It cannot be accounted for by electrochemical dissolution of UO_2 and therefore it is assumed that uraninite is a mixture of UO_3 and UO_2.

- Future research include the following include the development of rate expressions for the various gangue minerals (not assuming first order reactions) to improve the performance of

the empirical model as well as investigating the kinetics of pure brannerite. The k-values must be determined experimentally or calculated doing sum of square error minimisation instead of guessing k-values to fit the experimental data.

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Appendix A - Mineralogy

10.1 Composition formulas for various minerals

Mineral	Formula
Uraninite	UO_2
Brannerite	$(U,Th,Ca)[(Ti,Fe)_2O_6]$
Quartz	SiO_2
Muscovite	$KAl_3Si_3O_{10}(OH)_2$
Chlorite	$(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_8$
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
Pyrite	FeS_2
Carbonates	$Fe(CO_3)$, $Ca(CO_3)$
Albite	$mNaAlSi_3O_8$ with $nCaAl_2Si_2O_8$
K-Feldspar	$KAlSi_3O_8$
REE-phosphates	$(Ce,La,Y,Th)PO_4$, YPO_4
Copper	Cu
Carbon	C

10.2 Sample Splitting Procedure

10.2.1 Personal Protective Equipment Required

- Wear overalls or laboratory coat
- Gloves
- Safety goggles
- Safety shoes
- Dust musk
- Ensure that the area is in a safe condition to work and clean

10.2.2 Apparatus

- Rotary splitter (10 or 8 pot)
- Plastic bags
- Paint brush
- String
- Bottle marker (permanent)

10.2.3 Procedure

1) Clean the pots plus base of the splitter, hopper and trough
2) Place pots back on slots
3) Check the switch for the trough and the rotation if their functioning (If problems arises seek technical assistance)
4) Fill hopper with sample
5) Switch on for the rotation of pots
6) Switch on trough
7) Monitor the rate of addition by adjusting the vibration dial
8) At the end, put each fraction in a separate plastic bag
9) Label the plastic bag (as per labelling procedure)
10) Weigh each plastic bag and write the mass on it
11) Clean the whole splitter and the area

Appendix B - Standard Uranium Leaching

11.1 Standard working procedure

11.1.1 Personal Protective Equipment Required

- Safety overalls (acid resistant)
- Safety shoes/boots
- Safety gloves
- Safety goggles
- Face shield

11.1.2 Apparatus

- Water/Oil bath
- Over head stirrer
- Filter press
- Reactor vessel and lid
- Stop watch
- Spatula
- Chuck key
- Glass ware (beaker 1L; measuring cylinder)
- Weighing balance
- Filter papers
- Clamp
- H-stand
- Impeller (shaft)
- Wash bottle
- pH and Eh probes
- pH and Eh meters
- Sample containers
- Density meter
- Oven
- Sample dish/tray
- Baffles
- Sample labels
- Air flow meter
- Spurger
- Vacuum pump
- Syringe
- Buchner funnel and flask

11.1.3 Chemicals/Reagents required

- Uranium-bearing ore
- Sulphuric acid (H_2SO_4)
- De-ionised water
- Pyrolusite (MnO_2 ore)

11.1.4 Procedure

1) Connect the tubing from the water bath to the reactor vessel with the baffle inside the vessel
2) Clamp the overhead stirrer to the H-stand
3) Insert the shaft stirrer with the lid to the overhead stirrer using the chuck key
4) Pour water into the water bath and set it to required temperature (40°C – 60°C)
5) Weigh the material (ore = 1310g and water = 1015 ml)
6) Measure out the required amounts of dilute H_2SO_4 (1000 g/L) and MnO_2 ore
7) Add the water first followed by the ore into the reactor
8) Adjust the shaft until the lid clamps to the reactor. Ensure that the shaft is 1mm above the bottom of the reactor
9) Ensure that the shaft does not touch the baffle by manually stirring the shaft
10) Switch on the stirrer and slowly increase the speed (rpm) for proper agitation
11) Once the set temperature is reached, add the required quantity of diluted sulphuric acid (e.g. 33ml for 16.3kg/t addition and 20 ml for 12.8 kg/t addition) and switch on the stop watch
12) Set up the filtering apparatus by attaching the buchner funnel to the buchner flask
13) After 1hour take 170ml slurry sample using a syringe
14) Transfer the sampled pulp to the filtering apparatus described in step12
15) Switch off the vacuum pump and disconnect the filtering equipment
16) Transfer the filtrate to the beaker and weigh the wet cake, taking into consideration the mass of the filter paper
17) Measure the filtrate (volume or mass, density, Eh and pH)
18) Wash the filter cake and collect the wash water and do as in step 17
19) Perform a second wash and discard it
20) Remove the filter cake from the buchner funnel. Weigh and dry it
21) After 1.5 hours of reaction time, add the required amount of MnO_2 ore (e.g. 8.0g for 2kg/t addition and 12.0g for 3 kg/t addition)
22) Take samples after 3, 6 and 12 hours of reaction time. Collect a residue sample after 24 hours (requires that the test be stopped. Procedure is given below). The total number of samples for each test should be 5. Treat the samples as in steps 14 to 20.
23) Basic analysis that will be performed (specific analysis may be requested for certain tests)
24) Solid – U, Fe,
25) Solution – U, Fe^{2+}, Fe^{Total}, H^+, Mn^{2+}
26) At the end of the test switch off the stirrer and water bath

27) Dismount the stirrer and the lid
28) Transfer the final pulp into the beaker
29) Ensure the filter press is properly mounted and always check if it is working and clean by filtering water before the actual sample
30) Place weighed and labelled filter paper(s) on top of the base of the filter press
31) Pour the pulp into the filter press
32) Set the filter press and slowly open compressed air
33) Close the compressed air inlet valve and depressurize.
34) Dismount the filter press and weigh the final filtrate (PLS) and wash the cake as in steps 17-19
35) Clean up

11.1.5 Waste Management

Liquid and solid effluents must be kept separately and not be disposed off through the normal channels. Discharge bins must be provided to discard waste material, and they must be labeled correctly. At the end of the project all materials (fresh ore, solid and liquid) must be sent back to the client.

11.1.6 Task Risk Assessment

No	Specific Task/Activity	Potential Hazard / Conquences	Risk Rating	Control Measures (additional information can be attached)
1	Clamping the overhead stirrer to the H-stand.	Physical – struck by overhead stirrer (property damage)	L	Ensure that the clamp is tight enough before inserting the overhead stirrer
2	Insert the shaft stirrer to the overhead stirrer.	Physical – struck by shaft stirrer	L	Ensure that the shaft is in tact
3	Weighing Acid	Chemical – acid burn	M	Ensure that you wear proper PPE and face shield when dispensing acid
4	Exposure to hot oil/water	Physical – high temperature skin contact	M	Ensure that the tubing and clamp are in tact
5	Dismounting the stirrer	Physical – struck by the stirrer	L	See no.2
7	Transferring the final pulp into the beaker	Physical – exposure to high temperature pulp	M	Be cautious, wear proper PPE and work under extraction cupboard.

11.2 Standard Leaching Tests – Raw Data

Kopanang Raw Data for the Standard Tests*

Test ID	Temp	Acid	MnO2	Eh(1) [mV]	Eh(3) [mV]	Eh(4.5) [mV]	Eh(6) [mV]	Eh(10) [mV]	Eh(24) [mV]	pH(1)	pH(3)	pH(4.5)	pH(6)	pH(10)	pH(24)
Kop D	50	12.8	3	430	518	484	472	453	427	1.22	1.68	1.71	1.72	1.7	1.67
Kop E	40	9.9	2	442	544	519	500	480	458	1.16	1.42	1.49	1.51	1.56	1.69
Kop F	40	9.9	4	436	584	568	543	497	447	1.24	1.67	1.9	2.09	2.03	1.94
Kop G	60	9.9	2	401	460	441	428	413	387	1.33	1.66	1.64	1.64	1.67	1.82
Kop H	60	9.9	4	383	471	439	423	402	368	1.33	2.08	1.99	1.99	2.01	2.19
Kop M	40	16.3	4	413	564	540	510	480	463	1.03	1.21	1.27	1.32	1.36	1.42
Kop N	60	16.3	2	389	457	444	437	424	402	1.08	1.32	1.37	1.39	1.43	1.5
Kop O	50	12.8	3	396	502	474	464	450	426	1.15	1.57	1.59	1.59	1.63	1.64
Kop Q	60	16.3	4	380	480	460	450	434	408	0.88	1.24	1.26	1.27	1.27	1.33
Kop R	60	16.3	4	381	484	465	456	443	423	0.84	1.16	1.2	1.24	1.28	1.3
Kop S	50	12.8	3	379	493	473	464	451	433	1.01	1.44	1.46	1.48	1.51	1.53
Kop T	40	16.3	2	425	520	495	483	468	448	0.86	1.00	1.02	1.05	1.08	1.12
Kop 1	60	25	4	401	488	467	457	443	422	0.85	1.03	1.06	1.06	1.1	1.17

Noligwa Raw Data for the Standard Tests*

Test ID	Temp	Acid	MnO2	Eh(1) [mV]	Eh(3) [mV]	Eh(4.5) [mV]	Eh(6) [mV]	Eh(10) [mV]	Eh(24) [mV]	pH(1)	pH(3)	pH(4.5)	pH(6)	pH(10)	pH(24)
Noli A	40	16.3	2	414	483	468	460	450	430	1	1.17	1.2	1.23	1.3	1.42
Noli B	60	16.3	4	402	461	429	441	409	389	1.01	1.48	1.47	1.46	1.51	1.69
Noli C	50	12.8	3	404	473	456	446	428	394	1.11	1.54	1.58	1.61	1.63	1.7
Noli D	50	12.8	3	442	485	467	457	456	400	1.14	1.69	1.7	1.71	1.69	1.81
Noli E	40	9.9	2	435	506	482	471	457	433	1.22	1.59	1.64	1.71	1.75	1.79
Noli F	40	9.9	4	433	547	498	477	455	425	1.23	1.89	2.08	2.06	1.97	1.93
Noli G	60	9.9	2	402	436	416	403	376	360	1.33	1.71	1.72	1.81	1.94	2.13
Noli H	60	9.9	4	400	444	415	398	369	358	1.38	2.06	2.1	2.12	2.28	2.4
Noli I	40	16.3	4	422	544	502	486	466	442	0.91	1.14	1.22	1.26	1.33	1.42
Noli K	60	16.3	4	417	460	441	427	407	379	1.00	1.47	1.44	1.43	1.51	1.74
Noli J	60	16.3	2	409	453	440	434	416	380	1.06	1.36	1.4	1.43	1.49	1.62
Noli M	50	12.8	3	404	472	452	440	416	377	1.16	1.76	1.71	1.69	1.7	1.91
Noli 1	60	25	4	416	472	455	446	430	398	0.92	1.2	1.27	1.31	1.36	1.44

Moab Khotsong Raw Data for the Standard Tests*

Test ID	Temp	Acid	MnO2	Eh(1) [mV]	Eh(3) [mV]	Eh(4.5) [mV]	Eh(6) [mV]	Eh(10) [mV]	Eh(24) [mV]	pH(1)	pH(3)	pH(4.5)	pH(6)	pH(10)	pH(24)
Moab A	40	16.3	2	428	490	472	464	453	434	0.98	1.21	1.25	1.29	1.36	1.55
Moab B	60	16.3	4	326	441	427	414	392	383	1.22	1.96	1.93	1.91	1.91	2.25
Moab C	50	12.8	3	420	469	449	437	414	376	1.27	1.88	1.8	1.77	1.81	2.1
Moab D	50	12.8	3	411	473	455	443	421	381	1.21	1.77	1.76	1.74	1.74	1.96
Moab E	40	9.9	2	422	478	460	450	432	391	1.33	1.98	2	2	1.92	1.99
Moab F	40	9.9	4	425	508	476	461	433	393	1.23	2.1	2.17	2.06	1.98	2.15
Moab G	60	9.9	2	383	423	400	382	356	338	1.44	1.89	1.87	1.91	2.1	2.32
Moab H	60	9.9	4	390	435	402	384	361	330	1.39	2.23	2.26	2.33	2.43	2.7
Moab I	40	16.3	4	422	546	502	482	462	442	1.02	1.36	1.45	1.49	1.54	1.64
Moab J	60	16.3	2	404	451	437	427	401	366	1.18	1.54	1.55	1.55	1.6	1.84
Moab K	50	12.8	3	406	470	448	435	408	373	1.32	1.97	1.87	1.86	1.91	2.12
Moab 1	60	25	4	410	473	456	446	428	393	0.94	1.31	1.36	1.38	1.41	1.55

Kopanang Raw Data for the Standard Tests*

	Fe2+(1)	Fe2+(3)	Fe2+(4.5)	Fe2+(6)	Fe2+(10)	Fe2+(24)	Fe3+(1)	Fe3+(3)	Fe3+(4.5)	Fe3+(6)	Fe3+(10)	Fe3+(24)
Kop D	1.09	0.12	0.37	0.55	0.86	1.24	0.54	1.94	1.76	1.55	1.21	0.54
Kop E	0.89	0.05	0.05	0.21	0.43	0.84	0.73	1.82	1.87	1.80	1.62	1.30
Kop F	0.92	0.05	0.05	0.05	0.16	0.55	0.53	1.81	1.85	1.90	1.30	0.54
Kop G	0.41	0.7	0.87	1	1.22	0.21	1.79	1.30	0.81	0.63	0.44	1.53
Kop H	0.19	0.2	0.11	0.55	0.74	0.83	2.19	0.86	0.85	0.22	0.22	0.14
Kop M	1.29	0.05	0.05	0.12	0.47	0.97	0.45	2.32	2.74	2.66	2.42	2.42
Kop N	0.23	1.03	1.38	1.64	2.07	3.48	2.29	1.90	1.51	1.38	1.12	0.92
Kop O	1.77	0.25	0.62	0.86	1.2	2.07	0.27	2.28	1.99	1.91	1.51	1.02
Kop Q	2.41	0.65	1.18	1.51	2.16	3.29	0.22	2.74	2.18	1.86	1.51	0.99
Kop R	2.33	0.59	1.06	1.33	1.7	3.03	0.21	2.82	2.24	1.96	1.68	1.31
Kop S	1.97	0.33	0.69	0.89	1.2	2	0.15	2.25	2.02	1.81	1.51	1.21
Kop T	1.56	0.19	0.36	0.56	0.92	1.86	0.59	2.32	2.30	2.05	1.97	1.85
Kop 1	2.28	0.53	1.04	1.44	2.1	3.64	0.435	2.821	2.502	2.351	2.014	1.75

Noligwa Raw Data for the Standard Tests*

	Fe2+(1)	Fe2+(3)	Fe2+(4.5)	Fe2+(6)	Fe2+(10)	Fe2+(24)	Fe3+(1)	Fe3+(3)	Fe3+(4.5)	Fe3+(6)	Fe3+(10)	Fe3+(24)
Noli A	1.85	0.53	0.85	1.11	1.54	2.67	0.54	2.53	2.34	2.02	2.11	1.75
Noli B	2.89	1.27	1.85	2.25	2.81	3.91	2.42	2.89	2.28	1.38	1.17	0.34
Noli C	2.17	0.75	1.23	1.49	2.03	3.13	1.76	2.52	4.08	1.77	1.24	0.49
Noli D	1.49	0.49	0.91	1.17	1.6	2.58	1.15	2.59	2.18	1.79	1.01	0.39
Noli E	1.27	0.24	0.53	0.72	1.05	1.85	0.76	2.07	1.90	1.77	0.22	1.10
Noli F	1.28	0.05	0.26	0.49	0.74	1.36	0.64	2.42	2.18	1.71	1.00	0.52
Noli G	2.13	1.2	1.51	1.46	0.05	2.26	0.29	0.71	0.34	-0.30	1.82	0.04
Noli H	2.25	0.57	0.15	0.92	0.05	1.3	0.31	0.47	0.82	0.09	1.00	0.04
Noli I	1.48	0.06	0.29	0.53	1.01	2.15	0.58	2.90	2.70	2.59	2.33	2.19
Noli J	1.47	0.06	0.29	0.53	1.02	2.16	1.55	3.60	3.45	3.37	2.80	2.61
Noli K	3.59	4.347	3.9	3.762	2.94	3.792	1.96	1.67	0.00	1.02	0.84	0.72
Noli M	1.98	0.65	1.06	1.29	1.68	2.53	0.385	2.099	1.532	1.149	0.522	0.153
Noli 1	2.79	1.21	1.87	2.36	3.22	5.065	0.879	3.451	2.888	2.728	1.911	1.043

Moab Khotsong Raw Data for the Standard Tests*

	Fe2+(1)	Fe2+(3)	Fe2+(4.5)	Fe2+(6)	Fe2+(10)	Fe2+(24)	Fe3+(1)	Fe3+(3)	Fe3+(4.5)	Fe3+(6)	Fe3+(10)	Fe3+(24)
Moab B	4.4	1.56	1.77	2.03	2.3	2.8	0.05	1.43	0.89	0.62	0.28	0.34
Moab C	1.81	0.76	1.1	1.3	1.61	2.37	0.68	2.02	1.33	0.93	0.41	0.16
Moab D	1.93	0.68	1.07	1.28	1.65	2.54	0.46	2.25	1.69	1.18	0.61	0.24
Moab E	1.4	0.43	0.71	0.86	1.17	1.75	0.50	1.74	1.44	1.14	0.71	0.23
Moab F	1.39	0.14	0.39	0.57	0.91	1.41	0.54	2.27	1.80	1.49	0.62	0.20
Moab G	2.38	1.12	1.43	1.56	1.64	2.13	0.22	0.44	0.35	0.14	0.10	0.10
Moab H	2.34	0.51	0.67	0.75	0.12	1.15	0.30	0.33	0.13	0.08	0.75	0.06
Moab I	1.67	0.06	0.31	0.59	1.13	1.97	-0.52	2.95	2.97	2.71	2.83	2.29
Moab J	2.62	1.57	2.03	2.36	3	4.27	0.57	2.15	1.55	1.23	0.49	0.16
Moab K	1.94	0.61	0.95	1.13	1.49	2.06	0.35	1.92	1.11	0.74	0.36	0.14
Moab 1	2.9	1.1	1.705	2.17	2.87	4.57	0.7495	3.136	2.531	2.458	1.645	0.818

Kopanang Raw Data for the Standard Tests*

	H+(1)	H+(3)	H+(4.5)	H+(6)	H+(10)	H+(24)	Mn2+(1)	Mn2+(3)	Mn2+(4.5)	Mn2+(6)	Mn2+(10)	MN2+(24)
Kop D	7.53	2.29	2.19	2.17	2.33	2.68	0.0564	1.882	1.958	1.951	2.009	2.124
Kop E	8.28	4.42	3.75	3.64	3.17	2.33	0.0589	1.208	1.323	1.375	1.375	1.367
Kop F	6.85	2.52	1.42	0.85	1.09	1.56	0.0535	1.572	1.993	2.34	2.491	2.681
Kop G	7.3	2.29	2.55	2.55	2.43	1.58	0.0639	1.726	1.662	1.656	1.696	1.603
Kop H	5.83	0.72	1.03	1.01	1.52	1.09	0.0674	2.666	2.915	2.766	3.074	2.781
Kop M	12.3	7.8	6.71	6.07	5.39	4.78	0.0535	1.928	2.678	2.717	2.746	3.123
Kop N	11.7	5.71	5.33	5.06	4.65	4.27	0.0813	1.484	1.412	1.429	1.448	1.797
Kop O	9.08	2.92	2.82	2.88	2.77	2.31	0.0601	2.162	2.183	2.29	2.235	2.52
Kop Q	13.3	4.45	5.84	4.97	5.19	7.66	0.0702	2.678	2.681	2.726	2.884	3.31
Kop R	14.9	6.19	5.71	5.31	4.64	4.56	0.0705	2.894	2.833	2.718	2.633	3.256
Kop S	9.04	3.82	3.28	5.03	3.15	3.05	0.0595	1.937	2.002	2.015	1.969	2.357
Kop T	16	11.3	10.7	9.72	8.92	8.31	0.0622	1.322	1.378	1.329	1.353	1.592
Kop 1	20.8	12	10.65	10.6	9.82	8.31	0.0688	2.55	2.605	2.683	2.7505	3.141

Noligwa Raw Data for the Standard Tests*

	H+(1)	H+(3)	H+(4.5)	H+(6)	H+(10)	H+(24)	Mn2+(1)	Mn2+(3)	Mn2+(4.5)	Mn2+(6)	Mn2+(10)	MN2+(24)
Noli B	13.3	3.42	4.07	4.16	3.58	2.39	0.0927	2.945	3.191	3.058	3.372	3.229
Noli C	9.34	2.67	2.57	2.48	2.39	2.05	0.0778	2.094	3.389	2.086	2.101	2.483
Noli D	8.46	1.92	2.18	2.18	2.35	1.98	0.0525	2.053	2.14	2.065	2.071	2.436
Noli E	7.22	2.65	2.38	2.16	1.91	1.77	0.0456	1.332	1.376	1.373	692	1.588
Noli F	7.41	1.11	0.5	0.77	1.02	1.2	0.0435	2.308	2.613	2.591	2.461	2.99
Noli G	5.32	2.21	2.22	1.67	1.28	0.91	0.0509	1.385	1.435	1.242	1.415	1.64
Noli H	4.62	1.2	1.01	1.03	0.6	0.5	0.0518	2.699	2.684	2.749	2.679	3.295
Noli I	14.5	7.42	6.12	6.99	5.03	5.44	0.137	0.283	0.271	0.344	0.258	0.369
Noli J	11.4	5.85	5.34	4.42	4.08	3.06	0.0558	1.393	1.403	1.444	1.398	1.72
Noli K	12.8	3.84	4.46	4.39	3.83	2.36	0.0615	3.00	2.952	3.034	3.05	3.08
Noli M	7.85	1.76	2.13	2.15	2.4	1.45	0.0495	1.984	2.073	2.071	2.077	2.418
Noli 1	16.4	6.48	5.73	5.66	4.89	3.8	0.0599	2.619	2.575	2.703	2.685	3.242

Moab Khotsong Raw Data for the Standard Tests*

	H+(1)	H+(3)	H+(4.5)	H+(6)	H+(10)	H+(24)	Mn2+(1)	Mn2+(3)	Mn2+(4.5)	Mn2+(6)	Mn2+(10)	Mn2+(24)
Moab A	13.7	6.66	15.3	5.65	4.7	3.68	0.0553	1.282	1.362	1.336	1.348	1.589
Moab B	7.28	0.96	1.21	1.69	1.25	0.59	0.0812	2.649	2.598	2.743	2.753	3.404
Moab C	6.21	1.25	1.57	1.82	1.58	0.94	0.0568	2.018	2.036	2.073	2.03	2.434
Moab D	7.4	1.4	1.67	1.79	2.06	1.22	0.0563	2.074	2.114	2.027	2.1	2.469
Moab E	5.66	1.23	1.1	1.29	1.46	1.31	0.0504	1.357	1.377	1.357	1.413	1.616
Moab F	6.99	0.6	0.56	1.01	1.24	0.61	0.0499	2.477	2.631	2.917	2.731	3.199
Moab G	3.64	1.47	1.28	1.05	0.7	0.5	0.0585	1.272	1.538	1.433	1.414	1.715
Moab H	4.12	0.76	0.57	0.5	0.5	0.5	0.0587	2.687	2.656	2.667	2.665	3.248
Moab I	13.4	5.33	4.22	3.92	3.51	2.63	0.0539	2.42	2.719	2.717	3.036	2.983
Moab J	9.4	3.28	3.08	3.21	2.76	1.38	0.0633	1.481	1.414	1.419	1.438	1.707
Moab K	0.5	0.5	0.66	1.76	1.5	1.4	0.0524	2.003	1.963	1.95	2.031	2.254
Moab 1	15.2	5.31	4.97	4.82	4.65	3.265	0.0663	2.569	2.545	2.652	2.632	3.214

Kopanang Raw Data for the Standard Tests*

	U(ppm) (0)	U(ppm) (1)	U(ppm) (3)	U(ppm) (4.5)	U(ppm) (6)	U(ppm) (10)	U(ppm) (24)	U(g/L) (1)	U(g/L) (3)	U(g/L) (4.5)	U(g/L) (6)	U(g/L) (10)	U(g/L) (24)
Kop D	270	150	132	120	91.8	113	111	0.227	0.269	0.29	0.291	0.307	0.342
Kop E	337	166	120	128	106	111	108	0.238	0.296	0.302	0.306	0.289	0.294
Kop F	318	183	129	136	123	117.4	115	0.182	0.284	0.236	0.296	0.257	0.283
Kop G	293	152	128	119	108	121	93	0.242	0.284	0.298	0.291	0.304	0.299
Kop H	315	158	130	127	129	131	114	0.274	0.287	0.311	0.285	0.313	0.301
Kop M	285	176	110	104	124	107	42.30	0.112	0.246	0.284	0.262	0.271	0.332
Kop N	296	156	107	121	85.6	111	39.80	0.204	0.242	0.25	0.272	0.235	0.408
Kop O	250	184	124	117	129	119	44.80	0.166	0.217	0.295	0.195	0.256	0.264
Kop Q	289	138	105	111	91.2	96.4	28.10	0.272	0.308	0.305	0.333	0.339	0.411
Kop R	228	129	100	115	95.8	94.3	28.50	0.234	0.31	0.319	0.298	0.313	0.381
Kop S	282	197	126	117	110	107	42.00	0.164	0.297	0.296	0.312	0.303	0.353
Kop T		179	125	126	114	108	42.90	0.178	0.176	0.186	0.184	0.192	0.224
Kop 1	282	122	103	112	106	122	31.1	0.16	0.218	0.138	0.136	0.366	0.459

Noligwa Raw Data for the Standard Tests*

	U(ppm) (0)	U(ppm) (1)	U(ppm) (3)	U(ppm) (4.5)	U(ppm) (6)	U(ppm) (10)	U(ppm) (24)	U(g/L) (1)	U(g/L) (3)	U(g/L) (4.5)	U(g/L) (6)	U(g/L) (10)	U(g/L) (24)
Noli A	326	135	139	134	121	114	55.1	0.198	0.365	0.293	0.331	0.309	0.389
Noli B	314	159	129	119	181	125	54	0.459	0.31	0.405	0.418	0.327	0.369
Noli C	306	177	120	132	126	124	57	0.326	0.198	0.423	0.205	0.299	0.308
Noli D	354	149	128	107	124	126	64	0.266	0.288	0.265	0.305	0.293	0.43
Noli E	247	183	154	129	128	124	75	0.191	0.254	0.279	0.269	0.128	0.357
Noli F	349	180	143	151	165	135	82	0.187	0.199	0.226	0.214	0.233	0.264
Noli G	339	174	148	159	153	150	89	0.239	0.223	0.238	0.232	0.213	0.278
Noli H	373	180	150	159	147	151	105	0.203	0.294	0.223	0.246	0.271	0.236
Noli I	377	221	133	107	121	108	50	0.137	0.283	0.271	0.344	0.258	0.369
Noli J	371	136	121	117	117	108	51	0.261	0.251	0.262	0.312	0.295	0.343
Noli K	326	126	117	105	108	111	53.7	0.257	0.326	0.312	0.285	0.317	0.286
Noli M	341	147	133	128	129	120	62	0.199	0.277	0.253	0.282	0.307	0.381
Noli 1	320	153	130	124	124	109	46.4	0.248	0.358	0.241	0.325	0.356	0.399

Moab Khotsong Raw Data for the Standard Tests*

	U(ppm) (0)	U(ppm) (1)	U(ppm) (3)	U(ppm) (4.5)	U(ppm) (6)	U(ppm) (10)	U(ppm) (24)	U(g/L) (1)	U(g/L) (3)	U(g/L) (4.5)	U(g/L) (6)	U(g/L) (10)	U(g/L) (24)
Moab B	539	276	215	194	162	137	105	0.257	0.335	0.347	0.405	0.405	0.551
Moab C	467	197	218	204	193	176	105	0.322	0.353	0.449	0.368	0.397	0.442
Moab D	514	199	176	186	169	152	114	0.289	0.4	0.391	0.343	0.378	0.491
Moab E	423	277	207	206	198	183	123	0.25	0.382	0.345	0.338	0.403	0.434
Moab F	438	242	185	205	190	187	130	0.253	0.408	0.456	0.398	0.404	0.497
Moab G	388	219	197	192	187	186	113	0.34	0.387	0.424	0.359	0.461	0.469
Moab H	402	215	196	196	197	166	129	0.302	0.436	0.388	0.35	0.294	0.487
Moab I	519	349	239	216	208	179	164	0.296	0.297	0.447	0.352	0.504	0.397
Moab J	426	244	196	211	161	198	142	0.344	0.326	0.427	0.408	0.343	0.355
Moab K	411	239	204	171	172	147	104	0.246	0.176	0.261	0.192	0.262	0.298
Moab 1	377	176	149	156	160	153	56.7	0.34	0.343	0.357	0.37	0.34	0.283

* Values in parenthesis represent time when sample was taken (in hrs). Units for Fe^{2+}, Fe^{3+} , Mn^{2+} , and H^+ are g/l. H^+ is given as H_2SO_4.

11.3 Additional Tests – Raw Data

Raw Data for the Additional Tests*

	Temp	Acid	MnO2	Eh(1) [mV]	Eh(3) [mV]	Eh(4.5) [mV]	Eh(6) [mV]	Eh(10) [mV]	Eh(24) [mV]	pH(1)	pH(3)	pH(4.5)	pH(6)	pH(10)	pH(24)
Low Density															
Kopanang	50	12.8	3	415	572				446	0.92	1.11				1.26
Noligwa	50	12.8	3	427	530				431	0.94	1.22				1.43
Moab Khotsong	50	12.8	3	419	506				428	0.95	1.22				1.5
pH=1															
Kopanang	50		3	402	488	459			451	1.07	1.09	0.83			0.27
Noligwa	50		3	420	482	454			421	0.9	0.89	0.83			0.66
Moab Khotsong	50		3	411	474	460			419	0.66	0.8	0.85			0.86
Grind 60% -75um															
Kopanang	50	12.8	3	386	494	470	460	447	425	0.96	1.27	1.31	1.34	1.38	1.48
Noligwa	50	12.8	3	417	487	464	452	436	397	1.02	1.48	1.52	1.54	1.59	1.69
Moab Khotsong	50	12.8	3	406	476	457	446	428	389	1.04	1.59	1.63	1.64	1.71	1.82
Grind 40% -75um															
Kopanang	50	12.8	3	394	536	487	468	447	424	0.93	1.22	1.28	1.3	1.37	1.49
Noligwa	50	12.8	3	413	491	462	449	428	379	1	1.42	1.48	1.54	1.61	1.85
Moab Khotsong	50	12.8	3	407	495	464	450	429	383	1.03	1.49	1.55	1.63	1.71	1.81
Nitric Acid															
Kopanang	60		4	666	640	636	638	622	612	1.05	1.46	1.47	1.52	1.66	1.69
Noligwa	60		4	642	637	559	516	504	502	1.47	1.58	1.68	1.58	1.59	1.65
Moab Khotsong	60		4	637	635	630	537	517	502	1.51	1.59	1.64	1.368	1.66	1.65

Raw Data for the Additional Tests*

	Fe2+(1)	Fe2+(3)	Fe2+(4.5)	Fe2+(6)	Fe2+(10)	Fe2+(24)	Fe3+(1)	Fe3+(3)	Fe3+(4.5)	Fe3+(6)	Fe3+(10)	Fe3+(24)
Low Density												
Kopanang	0.91	0.05				1.26	0.236	1.5805				1.139
Noligwa	1.03	0.11				1.96	0.382	1.961				1.169
Moab Khotsong	1.17	0.21				2	0.295	1.814				0.967
pH=1												
Kopanang	1.75	0.46	0.93			1.99	0.267	2.0135	1.833			2.821
Noligwa	1.75	0.64	1.47			5.26	0.688	2.669	2.73			3.3315
Moab Khotsong	2	0.86	1.37			5.44	0.652	3.189	3.037			2.815
Grind 60% -75um												
Kopanang	1.72	0.43	0.65	0.89	1.32	2.22	0.033	1.6915	1.577	1.4	0.986	0.766
Noligwa	1.58	0.43	0.89	1.13	1.77	2.67	0.397	1.983	1.627	1.521	1.026	0.325
Moab Khotsong	1.77	0.66	1.11	1.32	1.79	2.695	0.258	1.817	1.896	1.385	0.735	0.173
Grind 40% -75um												
Kopanang	1.3	0.5	0.34	0.525	1.09	1.78	0.026	1.229	1.518	1.431	1.022	0.872
Noligwa	1.34	0.43	0.86	1.11	1.56	2.27	0.279	1.801	1.536	1.356	0.909	0.16
Moab Khotsong	1.39	0.38	0.67	1.08	1.535	2.42	0.272	1.7815	1.625	1.351	0.989	0.171
Nitric Acid												
Kopanang	0.5	0.5	0.5	0.5	0.5	0.5	3.62	4.553	3.964	3.966	3.672	3.415
Noligwa	0.05	0.05	0.05	0.05	0.4	0.41	4.952	4.218	4.035	4.123	3.566	3.7855
Moab Khotsong	0.05	0.05	0.05	0.05	0.05	0.34	4.903	4.255	4.2165	3.977	3.693	4.054

Raw Data for the Additional Tests*

	H+(1)	H+(3)	H+(4.5)	H+(6)	H+(10)	H+(24)	Mn2+(1)	Mn2+(3)	Mn2+(4.5)	Mn2+(6)	Mn2+(10)	Mn2+(24)
Low Density												
Kopanang	11.9	8.55				6.105	0.0319	1.617				2.271
Noligwa	12.6	6.75				4.1	0.0275	1.998				2.38
Moab Khotsong	11.6	6.61				3.29	0.0327	1.715				2.011
pH=1												
Kopanang	9.03	8.58	16.4			60.85	0.0621	1.629	1.566			2.159
Noligwa	14.2	15.1	17.3			27.1	0.0684	2.038	2.169			2.1875
Moab Khotsong	29.2	19.4	17.2			18.3	0.057	2.015	2.01			2.33
Grind 60% -75um												
Kopanang	11.2	5.45	4.93	4.55	3.95	2.96	0.0575	1.877	1.942	1.925	1.947	2.274
Noligwa	10	3.24	2.7	3.08	2.57	2.305	0.0465	1.922	2.001	2.0385	2.126	2.409
Moab Khotsong	9.3	2.55	2.58	2.19	1.7	1.42	0.0526	1.932	2.249	2.024	1.882	2.036
Grind 40% -75um												
Kopanang	12.7	6.07	5.52	5.27	4.25	3.4	0.0587	1.794	1.976	2.037	2.061	2.312
Noligwa	10.7	3.87	3.19	2.6	2.03	0.94	0.0473	1.998	2.0575	2.019	2.094	2.353
Moab Khotsong	10.2	3.27	2.46	2.6	2.07	1.27	0.0511	1.978	2.022	2.038	2.154	2.531
Nitric Acid												
Kopanang	7.2	2.65	3.32	2.97	2.41	2.83	0.0696	0.07265	0.0733	0.077	0.0786	0.107
Noligwa	2.79	2.28	2.03	1.94	1.7	1.51	0.0511	0.052	0.0524	0.0555	0.0568	0.0712
Moab Khotsong	2.33	2.16	1.92	1.49	1.48	1.52	0.0577	0.0591	0.063	0.062	0.0632	0.0788

Raw Data for the Additional Tests*

	U(ppm) (0)	U(ppm) (1)	U(ppm) (3)	U(ppm) (4.5)	U(ppm) (6)	U(ppm) (10)	U(ppm) (24)	U(g/L) (1)	U(g/L) (3)	U(g/L) (4.5)	U(g/L) (6)	U(g/L) (10)	U(g/L) (24)
Low Density													
Kopanang	266	137	91.45				25.4	0.138	0.172				0.202
Noligwa	274	140	89.65				36.3	0.153	0.177				0.202
Moab Khotsong	432	217	150				69.55	0.187	0.242				0.284
pH=1													
Kopanang	310	204	112	120			20.8	0.228	0.267	0.301			0.307
Noligwa	296	137	118	109			28.2	0.202	0.254	0.296			0.3445
Moab Khotsong	500	225	215	156			46.4	0.232	0.351	0.37			0.406
Grind 60% -75um													
Kopanang	277	198	121	115	111	188	52.7	0.172	0.264	0.246	0.296	0.272	0.349
Noligwa	338	150.5	125	131	123	115	71.7	0.225	0.231	0.285	0.275	0.281	0.308
Moab Khotsong	447	275	201	201	196	120	121	0.267	0.314	0.354	0.322	0.326	0.3695
Grind 40% -75um													
Kopanang	314	129	117	113	94.3	105	46.3	0.169	0.263	0.279	0.284	0.285	0.334
Noligwa	344	174	143	116	141.5	118	63.3	0.213	0.247	0.244	0.228	0.271	0.301
Moab Khotsong	508	348	154	192	126	166	146	0.231	0.311	0.348	0.379	0.68	0.439
Nitric Acid													
Kopanang	255	104	109	97.5	73.2	110	30.2	0.386	0.344	0.31	0.27	0.304	0.422
Noligwa	358	111	111	87.9	93.7	86.6	36.7	0.254	0.298	0.269	0.263	0.288	0.3555
Moab Khotsong	404	150	122	149	135	163.5	60	0.391	0.427	0.38	0.429	0.378	0.518

*Comments as in standard tests. Blank entries mean sample was not taken, generally by intent.

11.4 Particle Size Distribution Graph

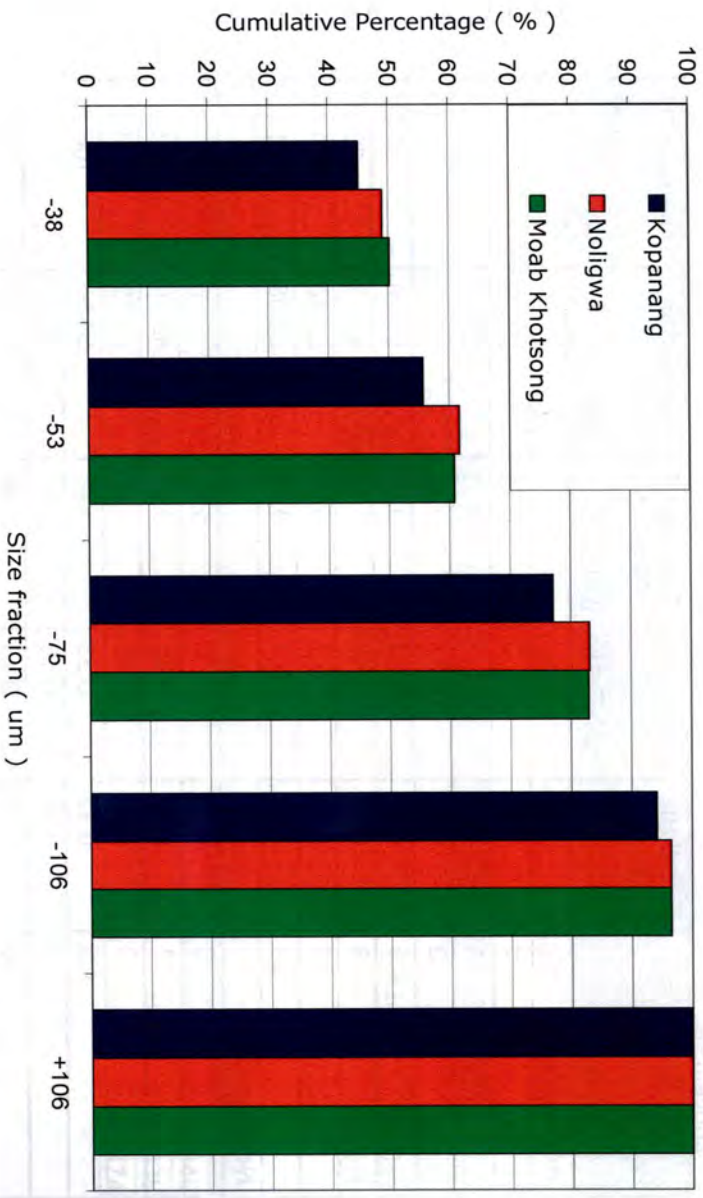

Figure 11.1 Particle size distribution of the milled ores

11.5 Indicative Uranium balance between Solution and Solids

(Only the results for one of the medium leaching conditions are shown)

	Solution (gU_3O_8/t)	Solid (gU_3O_8/t)	Calculated Head*** (gU_3O_8/t)	Dissolution* (%)	Dissolution** (%)
Kopanang O					
0	0.25	0	0.25	0	0
1	0.18	0.13	0.31	26.40	51.33
3	0.12	0.17	0.29	50.40	67.10
4.5	0.12	0.23	0.35	53.20	91.22
6	0.13	0.15	0.28	48.40	60.30
10	0.12	0.2	0.32	52.40	79.60
24	0.04	0.2	0.25	82.08	81.63
Noligwa C					
0	0.31	0	0.31	0	0
1	0.18	0.25	0.43	42.16	82.36
3	0.12	0.15	0.27	60.78	52.02
4.5	0.13	0.33	0.46	56.86	106.86
6	0.13	0.16	0.28	58.82	51.79
10	0.12	0.23	0.36	59.48	75.54
24	0.06	0.24	0.30	81.24	77.81
Moab Khotsong K					
0	0.41	0	0.41	0	0
1	0.24	0.19	0.43	41.85	46.27
3	0.20	0.14	0.34	50.36	33.10
4.5	0.17	0.20	0.37	58.39	49.09
6	0.17	0.15	0.32	58.15	36.11
10	0.15	0.20	0.35	64.23	49.28
24	0.10	0.23	0.33	74.70	56.05

*Dissolution based on measured head grade and measured solid concentration (ICP)

**Dissolution based on measured head grade (ICP) and solution concentration

***Calculated head grades based on a total uranium balance at each sample

It appears that the calculations that involve solution analysis frequently give non-sensical results. It was decided that percentage dissolutions in this work would be based on measured solid grades. The analytical department also has 'reference' uranium samples from Vaal River that were used to check the solids analysis. There is thus higher confidence in the solid measurements.

11.6 Chlorite Reaction Calculations

The concentrations of aluminium, magnesium and silica were measured for the 24 hour samples to get an indication of the extent of the chlorite reaction. Since magnesium is associated with the least amount of minerals [Schalkwyk and Gloy, 2006] it was decide to use it as basis for the calculations.

Chlorite reaction:

$$Mg_2Fe_2Al_{3.3}Si_{2.5}O_{10}(OH)_8+4H_2SO_4=2Mg^{2+}+1.7Fe^{2+}+0.3Fe^{3+}+3.3Al^{3+}+4SO_4^{2-}+2.5SiO_4^{2-}+8H_2O$$

Sample ID	Al(g/l)	Mr(Al)	Mg(g/l)	Mr(Mg)	Si(g/l)	Mr(Si)
Kop O6	0.551	26.982	0.197	24.305	0.439	28.086
Noli C6	0.903	26.982	0.294	24.305	0.646	28.086
Moab K6	0.678	26.982	0.271	24.305	0.517	28.086

Calculating the amount of chlorite dissolved using the chlorite reaction formula

Sample ID	Al(mol)	Al(mol)/3.3	Mg(mol)	Mg(mol)/2	Si(mol)	Si(mol)/2.5
Kop O6	0.02072734	0.00628101	0.00822691	0.004113	0.015865	0.006346
Noli C6	0.03396876	0.01029356	0.01227772	0.006139	0.023346	0.009338
Moab K6	0.02550478	0.00772872	0.01131722	0.005659	0.018684	0.007474

Predicted amount of chlorite dissolved based on Mg

Sample ID	Chlorite(mol)
Kop O6	0.00411345
Noli C6	0.00613886
Moab K6	0.00565861

The amount of Fe2+ and Fe3+ produced from chlorite

	Fe2+(mol)	Fe3+(mol)	Fe(total)(mol)
Kop O6	0.00699287	0.00123404	0.00822691
Noli C6	0.01043606	0.00184166	0.01227772
Moab K6	0.00961964	0.00169758	0.01131722

Amount of Fe in system dissolved from chlorite

Sample ID	Fe(total)(g)	Fe(g/l)
Kop O6	0.45944813	0.45265826
Noli C6	0.68567386	0.67554075
Moab K6	0.63203271	0.62269233

Based on the total amount of iron from chlorite the calculated amount of uranium that can possibly dissolve Fe:U=2:1

Sample ID	U(mol)	U(g)
Kop O6	0.00411345	0.97912546
Noli C6	0.00613886	1.46123292
Moab K6	0.00565861	1.34691878

The amount of uranium in the system

Sample ID	U(ppm)	U(g/g)
Kop O6	250	0.00025
Noli C6	306	0.000306
Moab K6	411	0.000411

For 1310g of ore

Sample ID	U(g)
Kop O6	0.3275
Noli C6	0.40086
Moab K6	0.53841

The calculation above shows that the iron from chlorite is sufficient to dissolve all the uranium in the ore. On the other hand, the total amount of Fe from chlorite (at most 0.7 g/l) is lower than the total amount of measured Fe, implying that there is another Fe source.

11.7 Indicative Fe Balance

Pyrolusite was added as oxidant 1.5 hours after the acid was added. Pyrolusite contains 29.3% MnO_2 and 36.5% Fe. (Only the results for medium leaching conditions are shown)

Kopanang O: (Amount Pyrolusite added: 12g)

Time	Measured Mn2+	% Dissolution (Mn)	Calculated Fe dissolved (assuming same dissolution as Mn)	Measured Fe in solution	Minimum Fe if Fe from pyrolusite indeed dissolved (1h+calculated Fe from pyrolusite)
1	0.0601	0	0	2.037	2.037
3	2.162	60.7	2.618	2.531	4.655
4.5	2.183	61.3	2.644	2.605	4.682
6	2.29	64.4	2.778	2.767	4.815
10	2.235	62.8	2.709	2.706	4.746
24	2.52	71.0	3.06	3.085	5.101

Noligwa C:(Amount Pyrolusite added: 12g)

Time	Measured Mn2+	%Dissolution (Mn)	Calculated Fe dissolved (assuming same dissolution as Mn)	Measured Fe in solution	Minimum Fe if Fe from pyrolusite indeed dissolved (1h+calculated Fe from pyrolusite)
1	0.0778	0	0	3.928	3.928
3	2.094	58.2	2.512	3.272	6.440
4.5	3.389	95.6	4.125	5.312	8.053
6	2.086	58.0	2.502	3.256	6.430
10	2.101	58.4	2.520	3.267	6.448
24	2.483	69.4	2.996	3.617	6.924

Moab Khotsong K:(Amount Pyrolusite added: 12g)

Time	Measured Mn2+	% Dissolution (Mn)	Calculated Fe dissolved (assuming same dissolution as Mn)	Measured Fe in solution	Minimum Fe if Fe from pyrolusite indeed dissolved (1h+calculated Fe from pyrolusite)
1	0.0524	0	0	2.285	2.285
3	2.003	56.3	2.430	2.532	4.715
4.5	1.963	55.2	2.380	2.062	4.665
6	1.95	54.8	2.364	1.87	4.649
10	2.031	57.1	2.465	1.846	4.750
24	2.254	63.6	2.743	2.202	5.028

From these results it seems that the Fe from pyrolusite does not leach to the same extent as Mn.

11.8 Leach residue mineralogy

*Table 11.1: Mineralogy of the bulk sample as well as the residue samples of the different tests for Kopanang ore].**

Noligwa	Bulk Mineralogy	24 h, 80% - 75µm, mid cond, H_2SO_4	24 h, 40% - 75µm, mid cond, H_2SO_4	24 h, 80% - 75µm, aggres cond, H_2SO_4	48 h, 80% - 75µm, aggres cond, H_2SO_4	24 h, 80% - 75µm, HNO_3	48 h, 80% - 75µm, HNO_3
Uraninite	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Brannerite	0.1	0.1	0.0	0.0	0.0	0.1	0.1
Quartz	70.2	63.7	67.1	63.8	68.0	61.6	67.9
Muscovite	10.1	12.3	11.3	12.6	13.0	11.6	10.7
Chlorite	2.0	0.5	0.7	0.5	0.8	0.5	0.5
Pyrophylite	9.7	11.6	10.1	10.7	6.2	11.7	10.0
Pyrite	1.3	0.5	0.5	0.5	0.9	0.1	0.2
Carbonates	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Albite	4..8	7.5	5.7	6.9	5.6	11.0	7.7
K-Feldspar	0.8	1.4	3.1	3.1	3.3	1.8	1.4
REE-phosphates	0.1	0.1	0.0	0.0	0.0	0.0	0.0
Other silicates	0.1	1.7	0.9	1.1	1.3	1.3	1.2
Other oxides	0.4	0.3	0.4	0.5	0.5	0.2	0.2
Copper	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon	0.2	0.3	0.2	0.3	0.4	0.1	0.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

*Table 11.2: Mineralogy of the bulk sample as well as the residue samples of the different tests for Noligwa ore.**

Noligwa	Bulk Mineralogy	24 h, 80% - 75µm, mid cond, H_2SO_4	24 h, 40% - 75µm, mid cond, H_2SO_4	24 h, 80% - 75µm, aggres cond, H_2SO_4	48 h, 80% - 75µm, aggres cond, H_2SO_4	24 h, 80% - 75µm, HNO_3	48 h, 80% - 75µm, HNO_3
Uraninite	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Brannerite	0.1	0.0	0.1	0.1	0.0	0.0	0.1
Quartz	73.3	67.9	72.8	71.4	71.6	72.5	76.8
Muscovite	11.3	14.8	11.9	12.1	13.8	12.1	11.0
Chlorite	3.2	1.2	1.3	0.8	1.0	1.1	0.5
Pyrophylite	2.5	3.3	2.6	2.7	2.2	3.0	2.3
Pyrite	2.5	1.2	1.7	1.1	1.2	0.9	1.0
Carbonates	0.2	0.1	0.0	0.0	0.0	0.0	0.0
Albite	5.1	6.7	4.8	5.9	4.3	6.4	4.9
K-Feldspar	0.4	1.9	2.1	2.6	3.6	1.1	0.3
REE-phosphates	0.2	0.0	0.1	0.0	0.0	0.1	0.1
Other silicates	0.2	2.0	1.8	2.3	1.2	2.4	2.5
Other oxides	0.4	0.4	0.4	0.4	0.6	0.2	0.3
Copper	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon	0.5	0.5	0.4	0.6	0.5	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 11.3: Mineralogy of the bulk sample as well as the residue samples of the different tests for Moab Khotsong ore.*

Moab Khotsong	Bulk Mineralogy	24 h, 80% - 75µm, mid cond, H_2SO_4	24 h, 40% - 75µm, mid cond, H_2SO_4	24 h, 80% - 75µm, aggres cond, H_2SO_4	48 h, 80% - 75µm, aggres cond, H_2SO_4	24 h, 80% - 75µm, HNO_3	48 h, 80% - 75µm, HNO_3
Uraninite	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Brannerite	0.1	0.1	0.0	0.1	0.0	0.1	0.1
Quartz	79.8	67.1	71.2	73.2	72.1	73.1	71.7
Muscovite	8.2	12.8	11.9	11.8	13.4	11.7	12.9
Chlorite	3.6	1.3	1.6	1.3	1.1	1.1	1.1
Pyrophylite	1.1	3.1	2.0	2.0	1.7	2.5	2.7
Pyrite	2.8	1.3	1.6	1.4	1.2	0.8	0.8
Carbonates	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Albite	1.9	7.6	5.0	4.8	4.3	6.1	6.3
K-Feldspar	1.3	2.2	3.8	1.9	3.6	1.1	1.0
REE-phosphates	0.1	0.1	0.0	0.0	0.0	0.1	0.1
Other silicates	0.3	3.3	1.8	2.5	1.6	2.9	2.5
Other oxides	0.2	0.4	0.4	0.5	0.5	0.2	0.3
Copper	0.1	0.0	0.0	0.0	0.0	0.0	0
Carbon	0.3	0.7	0.7	0.5	0.5	0.3	0.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

**Uraninite and brannerite mass fractions are inaccurate on a bulk mineralogy scale. The values should probably be re-normalised to quartz (not expected to dissolve) to compare feed and residue bulk mineralogies.*

Appendix C – Forward and Reverse Uranium Leaching

12.1 Forward Leaching – Raw Data

Table 12.1: Kopanang Forward Leaching Results

Kopanang Forward Leaching (KFL) Results								
Head Grade				**7.99**				**8.29**
Time (hrs)	**sample**	**Au (mg/l)**	**CN- (mg\l)**	**Au (g/t)**	**sample**	**Au (g/l)**	**CN- (mg\l)**	**Au (g/t)**
2	KFL -1.1	6.52	227	3.48	KFL -2.1	7.9	320	7.54
4	KFL -1.2	6.9	178	1.61	KFL -2.2	6.08	146	1.35
6	KFL -1.3	8.04	192	1.15	KFL -2.3	7.88	200	0.98
8	KFL -1.4	8.24	183	0.77	KFL -2.4	7.94	48.7	0.71
24	KFL -1.5	10.9	141	0.48	KFL -2.5	10.3	175	0.64

Table 12.2: Noligwa Forward Leaching Results

Noligwa Forward Leaching (NFL)Results								
Head Grade				**11.6**				**10.6**
Time (hrs)	**sample**	**Au (mg/l)**	**CN- (mg\l)**	**Au (g/t)**	**sample**	**Au (g/l)**	**CN- (mg\l)**	**Au (g/t)**
2	NFL -1.1	0.6	21.8	9.27	NFL -2.1	7.6	91.3	1.83
4	NFL -1.2	5.18	67.4	3.37	NFL -2.2	8.42	129	1.6
6	NFL -1.3	6.7	95	1.11	NFL -2.3	8.98	266	1.26
8	NFL -1.4	6.92	200	1	NFL -2.4	9.2	243	0.86
24	NFL -1.5	8.12	106	0.69	NFL -2.5	9.82	233	0.675

Table 12.3: Moab Khotsong Forward Leaching Results

Moab Khotsong Forward Leaching (MKFL) Results								
Head Grade				**12.6**				**11.7**
Time (hrs)	**sample**	**Au (mg/l)**	**CN- (mg\l)**	**Au (g/t)**	**sample**	**Au (g/l)**	**CN- (mg\l)**	**Au (g/t)**
2	MKFL -1.1	10.5	42.9	3.05	MKFL -2.1	9.48	162	2.88
4	MKFL -1.2	11.3	105	1.19	MKFL -2.2	12	220	1.4
6	MKFL -1.3	11.9	163	1.17	MKFL -2.3	13.2	181	0.99
8	MKFL -1.4	12.4	59.7	0.97	MKFL -2.4	12.6	153	0.93
24	MKFL -1.5	14	45.8	0.84	MKFL -2.5	16.1	37	0.71

12.2 Reverse Leaching – Raw Data

Table 12.4: Kopanang Reverse Leaching Results

Kopanang Reverse Leaching (KRL) Results								
Head Grade				**7.66**				**8.48**
Time (hrs)	**sample**	**Au (mg/l)**	**CN- (mg\l)**	**Au (g/t)**	**sample**	**Au (g/l)**	**CN- (mg\l)**	**Au (g/t)**
2	KRL -1.1	7.32	214	0.99	KRL -2.1	7.36	238	2.07
4	KRL -1.2	6.81	173	0.4	KRL -2.2	7.4	202	1.57
6	KRL -1.3	6.96	169	0.54	KRL -2.3	6.08	133	0.25
8	KRL -1.4	7.4	164	0.185	KRL -2.4	7.4	170	0.28
24	KRL -1.5	8.88	109	0.12	KRL -2.5	9.44	123	0.13

Table 12.5: Noligwa Reverse Leaching Results

Noligwa Reverse Leaching (NRL) Results								
Head Grade				**9.705**				**7.96**
Time (hrs)	**sample**	**Au (mg/l)**	**CN- (mg\l)**	**Au (g/t)**	**sample**	**Au (g/l)**	**CN- (mg\l)**	**Au (g/t)**
2	NRL -1.1	7.56	198	1.42	NRL -2.1	7.62	185	0.98
4	NRL -1.2	7.96	179	0.8	NRL -2.2	8.22	48.9	0.48
6	NRL -1.3	7.7	191	0.32	NRL -2.3	7.66	156	0.43
8	NRL -1.4	8.02	294	0.32	NRL -2.4	7.32	67.8	0.36
24	NRL -1.5	10.3	344	0.27	NRL -2.5	9.7	76.2	0.23

Table 12.6: Moab Khotsong Reverse Leaching Results

Moab Khotsong Reverse Leaching (MKRL) Results								
Head Grade				**12.7**				**14**
Time (hrs)	**sample**	**Au (mg/l)**	**CN- (mg\l)**	**Au (g/t)**	**sample**	**Au (g/l)**	**CN- (mg\l)**	**Au (g/t)**
2	MKRL -1.1	9.31	17.4	2.65	MKRL -2.1	10.3	154	1.78
4	MKRL -1.2	10.7	75.9	1.65	MKRL -2.2	10.6	200	0.92
6	MKRL -1.3	11.1	52.1	1.05	MKRL -2.3	11.1	165	0.56
8	MKRL -1.4	11	182	0.67	MKRL -2.4	11.2	150	0.38
24	MKRL -1.5	14.7	26	0.31	MKRL -2.5	12.6	102	0.27

Appendix D – Uranium Diagnostic Leaching

13.1 Operating Procedure – Auto Titrator

1) For the setup of the leaching experiment follow the same working procedure as describe in Appendix B – Section 11.1.4.
2) The Radiometer TitraMaster 85 was used for the experiments
3) Install TitraMaster 85 Data Collector on the computer to be connected to the auto titrator
4) Install update version TitraMaster Update v4.0. msi (www.radiometer-analytical.com)
5) Connect the computer to the auto titrator
6) To create the method it is necessary to go into the supervisor mode
7) Go to electrode tab (third tab)
8) Create or select the electrode to be used for the analyses
9) Select temperature sensor
10) Specify if electrode calibration is required (or not) depending on if pH or Eh electrode will be used
11) Connect the electrode
12) Go to reagent tab (second tab)
13) Create or select the reagents to be used for the analyses
14) Specify is reagent calibration is required (or not).
15) Install the reagent
16) It is necessary to set the electrode and reagent setting before programming the method
17) In method/sequence tab choose Method library press 4.
18) Press 1 to create a new method
19) Enter the parameters required to calculate the results
20) Insert the electrode, reagent probes and temperature sensor into the reactor
21) Take care that the impeller inside the reactor does not touch the glass electrode
22) It is recommended that the probes are strapped to the baffle inside the reactor using cable ties
23) Due to the nature of the reagents used it is recommended to cover the cables of the auto titrator with teflon type and silicon
24) When finished select/run the method or pre-programmed application in the method/sequence tab

13.2 Diagnostic Leaching – Raw Data

Table 13.1: Solid and liquid analysis of various diagnostic leaching tests for Kopanang ore

	Time (h)	Leaching Agent	Solid Fe (ppm)	Solid U (ppm)	Liquid Fe (ppm)	Liquid Mn (ppm)	Liquid U (ppm)
Kopanang A (Head Grade)			12700	234.1			
Kopanang A	24	Aggressive Leaching (without oxidant)	8011	38.28	5005.5	109.8	376.6
Kopanang G	+- 7	HNO_3 Overdose	1229	4.77	6274.5	24.2	53.7
Kopanang D (Head Grade)			8071	328.5			
Kopanang D	24	Aggressive Leaching			673.8	2913.5	401.8
Kopanang E	48	Aggressive Leaching			1718.5	2988.7	127.0
Kopanang F	72	Aggressive Leaching	14010	20.92	1965.8	3444.8	142.8
Kopanang B (Head Grade)			8778	357.3			
Kopanang B1	1	Constant Eh 500mV, H_2O_2	6259	99.25	4075.4	91.2	434.3
Kopanang B2	3	Constant Eh 500mV, H_2O_2	8711	77.47	2991.5	95.3	356.7
Kopanang B3	5	Constant Eh 500mV, H_2O_2	8886	55.48	2856.9	98.1	361.0
Kopanang B4	10	Constant Eh 500mV, H_2O_2	8571	65.59	5157.6	104.8	420.5
Kopanang B5	24	Constant Eh 500mV, H_2O_2	8944	24.94	6222.4	121.7	433.2
Kopanang C (Head Grade)			12690	243.6			
Kopanang C1	1	Constant Eh 700mV, HNO_3	4004	93.45	6639.0	76.6	376.9
Kopanang C2	3	Constant Eh 700mV, HNO_3	3917	103.3	9525.5	93.7	496.8
Kopanang C3	5	Constant Eh 700mV, HNO_3	6019	73.34	10394.2	97.6	383.9
Kopanang C4	10	Constant Eh 700mV, HNO_3	2726	88	12343.3	111.3	418.6
Kopanang C5	24	Constant Eh 700mV, HNO_3	1248	21.17	16504.6	167.1	697.2

Table 13.2: Solid and liquid analysis of various diagnostic leaching tests for Noligwa ore

	Time (h)	Leaching Agent	Solid Fe (ppm)	Solid U (ppm)	Liquid Fe (ppm)	Liquid Mn (ppm)	Liquid U (ppm)
Noligwa A (Head Grade)			16640	320.5			
Noligwa A	24	Aggressive Leaching (without oxidant)	12790	57.23	4413.3	103.3	402.8
Noligwa G	+- 7	HNO_3 Overdose	1296	4.891	15819.3	56.0	67.6
Noligwa D (Head Grade)			16430	389.8			
Noligwa D	24	Aggressive Leaching			1841.6	3288.9	379.5
Noligwa E	48	Aggressive Leaching			2219.5	3923.5	158.6
Noligwa F	72	Aggressive Leaching	25620	21.44	1616.4	3039.4	150.0
Noligwa B (Head Grade)			24450	306.6			
Noligwa B1	1	Constant Eh 500mV, H_2O_2	11630	82.44	2389.7	77.7	396.7
Noligwa B2	3	Constant Eh 500mV, H_2O_2	12640	107.2	2143.1	82.2	458.2
Noligwa B3	5	Constant Eh 500mV, H_2O_2	17480	76.6	2021.6	84.1	414.7
Noligwa B4	10	Constant Eh 500mV, H_2O_2	12430	77.28	2411.3	85.9	396.2
Noligwa B5	24	Constant Eh 500mV, H_2O_2	18590	62.77	2946.3	103.5	454.6
Noligwa C (Head Grade)			17610	353.8			
Noligwa C1	1	Constant Eh 700mV, HNO_3	8325	103	12599.1	82.8	449.9
Noligwa C2	3	Constant Eh 700mV, HNO_3	9146	111.1	8632.0	86.8	466.9
Noligwa C3	5	Constant Eh 700mV, HNO_3	8006	128.8	7822.0	87.4	479.6
Noligwa C4	10	Constant Eh 700mV, HNO_3	10160	95.81	7745.3	97.1	420.8
Noligwa C5	24	Constant Eh 700mV, HNO_3	15830	38.48	12973.7	136.3	661.4

Table 13.3: Solid and liquid analysis of various diagnostic leaching tests for Moab Khotsong ore

	Time (h)	Leaching Agent	Solid Fe (ppm)	Solid U (ppm)	Liquid Fe (ppm)	Liquid Mn (ppm)	Liquid U (ppm)
Moab Khotsong A (Head Grade)			15740	444.9			
Moab Khotsong A	24	Aggressive Leaching (without oxidant)	19480	81.6	4923.5	154.5	701.6
Moab Khotsong G	+- 7	HNO_3 Overdose	1331	6.16	12999.0	55.0	56.9
Moab Khotsong D (Head Grade)			16170	602.5			
Moab Khotsong D	24	Aggressive Leaching			1791.6	2860.8	645.5
Moab Khotsong E	48	Aggressive Leaching			2128.0	2895.4	185.0
Moab Khotsong F	72	Aggressive Leaching	22710	43.8	1640.9	2906.3	138.1
Moab Khotsong B (Head Grade)			21420	475.3			
Moab Khotsong B1	1	Constant Eh 500mV, H_2O_2	21140	141.6	2498.6	103.3	614.1
Moab Khotsong B2	3	Constant Eh 500mV, H_2O_2	20910	140.6	2395.4	111.0	667.7
Moab Khotsong B3	5	Constant Eh 500mV, H_2O_2	21720	164	2280.2	118.5	647.3
Moab Khotsong B4	10	Constant Eh 500mV, H_2O_2	21600	154	2157.6	129.8	665.5
Moab Khotsong B5	24	Constant Eh 500mV, H_2O_2	14330	65.15	2476.3	159.0	739.7
Moab Khotsong C (Head Grade)			18020	649.4			
Moab Khotsong C1	1	Constant Eh 700mV, HNO_3	8644	93.19	12496.7	131.9	637.3
Moab Khotsong C2	3	Constant Eh 700mV, HNO_3	9509	177.5	9643.6	142.3	727.2
Moab Khotsong C3	5	Constant Eh 700mV, HNO_3	12360	110.9	8923.1	144.1	669.4
Moab Khotsong C4	10	Constant Eh 700mV, HNO_3	13220	115.5	9152.8	161.1	728.4
Moab Khotsong C5	24	Constant Eh 700mV, HNO_3	12060	34.48	13877.3	247.1	1166.2

13.3 Diagnostic Leaching - Mineralogical Analyses

Table 13.4: Bulk mineralogy analysis of residue samples for different potential conditions

	Kopanang Natural Potential	Kopanang 500mV	Kopanang 700mV	Noligwa Natural Potential	Noligwa 500mV	Noligwa 700mV	Moab Khotsong Natural Potential	Moab Khotsong 500mV	Moab Khotsong 700mV
Uraninite	0.063	0.064	0.060	0.130	0.093	0.100	0.094	0.113	0.069
Brannerite	0.044	0.054	0.031	0.044	0.050	0.048	0.065	0.062	0.027
U_Phosphate	0.002	0.002	0.000	0.000	0.000	0.000	0.007	0.007	0.000
USi_Th	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.000
Gold	0.000	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.011
Galena	0.017	0.005	0.021	0.010	0.005	0.010	0.006	0.006	0.005
Gersdorffite	0.004	0.000	0.000	0.012	0.000	0.000	0.005	0.004	0.000
Pyrite	1.763	1.785	0.569	3.663	3.175	0.405	3.591	3.240	0.200
Arsenopyrite	0.004	0.004	0.000	0.024	0.018	0.000	0.041	0.030	0.004
Chalcopyrite	0.021	0.015	0.003	0.008	0.009	0.011	0.018	0.018	0.005
Millerite	0.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sphalerite	0.050	0.038	0.029	0.064	0.024	0.024	0.049	0.031	0.026
Carbonate	0.009	0.011	0.008	0.025	0.006	0.022	0.025	0.011	0.023
Apatite	0.004	0.019	0.000	0.011	0.010	0.000	0.012	0.004	0.000
REE_ Phosphate	0.053	0.076	0.073	0.063	0.062	0.042	0.075	0.065	0.053
Quartz	83.48	82.876	83.703	81.57	82.24	83.822	80.635	81.045	83.511
Feldspar	2.034	1.971	2.180	2.041	2.217	2.675	2.412	2.274	2.944
Fe-silicate	0.777	0.696	1.126	1.261	1.523	1.481	1.857	2.102	1.958
Mica	4.734	5.447	4.938	6.448	6.265	7.154	6.627	6.191	6.938
Zircon	0.134	0.126	0.103	0.060	0.093	0.080	0.064	0.127	0.068
Chlorite	0.758	0.644	0.628	1.520	1.388	1.391	1.544	1.417	1.460
Pyrophyllite	4.921	5.034	5.239	1.248	1.454	1.507	1.137	1.118	1.328
Chromite	0.024	0.018	0.053	0.015	0.018	0.027	0.004	0.012	0.009
Rutile	0.069	0.072	0.059	0.091	0.093	0.069	0.092	0.073	0.078
Titanite	0.249	0.311	0.281	0.323	0.276	0.242	0.275	0.308	0.272
Carbon	0.139	0.121	0.057	0.204	0.171	0.042	0.322	0.190	0.056
FeO	0.258	0.216	0.550	0.612	0.411	0.534	0.577	0.514	0.374
Others	0.390	0.386	0.288	0.537	0.400	0.309	0.457	1.036	0.582
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 13.5: Bulk mineralogy of residue sample for different leaching times

	Kopanang Aggressive H_2SO_4 24h	Kopanang Aggressive H_2SO_4 48h	Kopanang Aggressive H_2SO_4 72h	Noligwa Aggressive H_2SO_4 24h	Noligwa Aggressive H_2SO_4 48h	Noligwa Aggressive H_2SO_4 72h	Moab Khotsong Aggressive H_2SO_4 24h	Moab Khotsong Aggressive H_2SO_4 48h	Moab Khotsong Aggressive H_2SO_4 72h
Uraninite	0.089	0.121	0.078	0.112	0.091	0.064	0.112	0.085	0.053
Brannerite	0.049	0.009	0.052	0.073	0.063	0.030	0.040	0.038	0.039
U_Phosphate	0.003	0.000	0.003	0.004	0.000	0.000	0.002	0.000	0.000
USi_Th	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.000
Gold	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.014
Galena	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.005	0.006
Gersdorffite	0.000	0.000	0.000	0.006	0.000	0.000	0.007	0.000	0.000
Pyrite	1.661	1.473	1.394	3.461	3.546	2.847	3.263	3.371	3.299
Arsenopyrite	0.000	0.005	0.016	0.039	0.000	0.040	0.050	0.046	0.024
Chalcopyrite	0.000	0.000	0.008	0.032	0.004	0.011	0.014	0.021	0.024
Millerite	0.004	0.000	0.000	0.006	0.000	0.005	0.000	0.000	0.000
Sphalerite	0.041	0.018	0.029	0.045	0.032	0.027	0.041	0.055	0.090
Carbonate	0.046	0.059	0.099	0.064	0.038	0.225	0.049	0.061	0.038
Apatite	0.002	0.003	0.000	0.017	0.000	0.000	0.012	0.000	0.003
REE_Phosphate	0.099	0.065	0.093	0.048	0.052	0.043	0.095	0.035	0.041
Barite	0.003	0.000	0.004	0.000	0.000	0.000	0.000	0.003	0.007
Quartz	81.179	79.540	80.390	79.467	78.604	78.841	79.690	80.117	80.108
Feldspar	2.060	2.058	1.903	2.215	2.074	2.192	2.204	2.365	2.367
Fe-silicate	1.444	1.801	1.951	2.159	2.359	2.774	2.528	2.580	2.683
Mica	5.059	5.336	5.247	6.608	6.451	6.884	6.605	5.996	5.207
Zircon	0.040	0.133	0.073	0.073	0.086	0.049	0.045	0.050	0.086
Chlorite	0.996	0.569	0.648	1.603	1.204	1.033	1.578	1.381	1.306
Pyrophyllite	5.006	5.430	4.984	1.296	1.270	1.466	1.117	1.058	0.935
Chromite	0.032	0.016	0.025	0.050	0.018	0.020	0.020	0.010	0.051
Rutile	0.073	0.071	0.063	0.065	0.072	0.048	0.069	0.057	0.084
Titanite	0.288	0.249	0.327	0.235	0.255	0.260	0.298	0.286	0.238
Carbon	0.127	0.103	0.085	0.238	0.148	0.209	0.241	0.209	0.242
FeO	1.196	1.229	1.778	1.398	1.847	1.758	1.027	1.502	2.494
Others	0.501	1.710	0.750	0.687	1.784	1.173	0.878	0.671	0.560
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 13.6: Mineralogy analysis of residue sample after nitric acid digestion

	Kopanang Nitric Acid Digestion	Noligwa Nitric Acid Digestion	Moab Khotsong Nitric Acid Digestion
Uraninite	0.047	0.037	0.043
Brannerite	0.013	0.017	0.013
U_Phosphate	0.000	0.000	0.004
USi_Th	0.000	0.004	0.000
Gold	0.000	0.000	0.000
Galena	0.000	0.000	0.005
Gersdorffite	0.000	0.000	0.000
Pyrite	0.050	0.033	0.046
Arsenopyrite	0.000	0.000	0.000
Chalcopyrite	0.013	0.011	0.006
Millerite	0.000	0.000	0.000
Sphalerite	0.015	0.015	0.023
Carbonate	0.005	0.004	0.009
Apatite	0.004	0.002	0.002
REE_Phosphate	0.066	0.070	0.040
Barite	0.000	0.000	0.000
Quartz	84.190	87.456	89.165
Feldspar	2.034	2.226	2.429
Fe-silicate	0.246	0.285	0.276
Mica	5.842	7.223	5.617
Zircon	0.085	0.094	0.078
Chlorite	0.054	0.076	0.041
Pyrophyllite	6.126	1.419	1.030
Chromite	0.028	0.010	0.074
Rutile	0.085	0.074	0.059
Titanite	0.298	0.325	0.366
Carbon	0.058	0.050	0.026
FeO	0.203	0.201	0.177
Others	0.540	0.369	0.472
Total	100.00	100.00	100.00

Table 13.7: Percentage brannerite liberation and percentage of brannerite with 5 and 10 % surface exposure for the residue samples after different leaching times for Kopanang, Noligwa and Moab Khotsong ore

	Kopanang Aggressive H_2SO_4 24h	Kopanang Aggressive H_2SO_4 48h	Kopanang Aggressive H_2SO_4 72h	Noligwa Aggressive H_2SO_4 24h	Noligwa Aggressive H_2SO_4 48h	Noligwa Aggressive H_2SO_4 72h	Moab Aggressive H_2SO_4 24h	Moab Khotsong Aggressive H_2SO_4 48h	Moab Khotsong Aggressive H_2SO_4 72h
Liberation	19.55	41.56	30.64	36.88	21.87	13.00	27.50	24.02	54.59
Free surface >5%	96.10	90.69	100.00	89.52	98.57	96.03	95.63	95.40	88.66
Free surface >10%	92.84	59.19	97.60	84.93	85.73	86.85	80.77	87.35	85.42

Table 13.8: Percentage uraninite liberation and percentage of uraninite with 5 and 10 % surface exposure for the residue samples after different leaching times for Kopanang, Noligwa and Moab Khotsong ore

	Kopanang Aggressive H_2SO_4 24h	Kopanang Aggressive H_2SO_4 48h	Kopanang Aggressive H_2SO_4 72h	Noligwa Aggressive H_2SO_4 24h	Noligwa Aggressive H_2SO_4 48h	Noligwa Aggressive H_2SO_4 72h	Moab Aggressive H_2SO_4 24h	Moab Khotsong Aggressive H_2SO_4 48h	Moab Khotsong Aggressive H_2SO_4 72h
Liberation	21.20	1.81	79.82	15.90	15.62	8.90	4.70	1.54	6.58
Free surface >5%	89.66	78.67	98.09	86.50	94.18	91.21	86.48	96.44	83.63
Free surface >10%	83.07	75.06	97.83	53.21	90.57	79.36	70.95	87.24	81.72

Table 13.9: Grain size distribution of brannerite particles for Kopanang, Noligwa and Moab Khotsong residue samples after leaching tests at different potentials

Size	Kopanang Natural Potential	Kopanang 500mV	Kopanang 700mV	Noligwa Natural Potential	Noligwa 500mV	Noligwa 700mV	Moab Khotsong Natural Potential	Moab Khotsong 500mV	Moab Khotsong 700mV
75.00									
63.00				25.46				33.21	
53.00									
45.00									
38.00	35.46			15.61				10.67	
32.00	23.30							16.66	
27.00		26.02		14.00	30.62		7.51		
22.00	10.27							4.38	19.79
19.00				1.69	7.38	23.10	3.70		
16.00	6.54	15.68			13.17		5.48	3.38	7.28
13.50				6.89	7.76	11.08	11.60	6.71	5.61
11.40	5.88	4.88		7.31	6.56		8.97	1.10	12.54
9.60	6.52	8.54		3.80	3.66	5.74	8.11	4.05	10.50
8.10	3.63	18.30	13.88	6.85	6.29	8.90	4.49	4.03	3.01
6.80	3.95	2.42	25.54	3.61	5.08	13.39	9.73	3.06	11.63
5.70		8.15	11.44	3.12	2.80	7.02	8.66	3.72	9.59
4.80	2.19	2.82	7.76	3.57	4.78	1.32	8.39	2.54	3.53
4.10	0.78	1.38	8.34	3.24	2.73	8.94	6.44	1.66	3.67
3.40	0.40	4.06	6.37	1.46	4.07	7.19	5.41	1.74	4.06
2.90	0.39	1.06	9.12	0.85	2.35	4.46	3.68	1.37	2.47
2.40	0.17	0.41	5.30	0.70	1.06	2.39	3.22	0.69	1.72
2.00	0.22	3.77	5.38	0.74	0.67	2.52	1.76	0.34	1.10
1.75	0.13	0.36	1.58	0.22	0.28	0.90	0.76	0.20	1.22
1.45	0.07	0.73	2.98	0.34	0.29	1.15	1.20	0.22	0.97
1.20	0.03	0.50	0.25	0.20	0.12	0.55	0.28	0.14	0.56
1.00	0.01	0.33	1.21	0.16	0.16	0.61	0.36	0.04	0.22
0.87	0.02	0.16	0.16	0.06	0.10	0.27	0.14	0.04	0.35
0.73	0.02	0.43	0.09	0.11	0.05	0.27	0.12	0.06	0.17
0.62			0.12			0.12		0.00	
0.52			0.35			0.08			
0.00			0.15	0.00			0.00	0.01	

Table 13.10: Grain size distribution of brannerite particles for Kopanang, Noligwa and Moab Khotsong residue samples for leaching tests at different leaching times

Size	Kopanang Aggressive H_2SO_4 24h	Kopanang Aggressive H_2SO_4 48h	Kopanang Aggressive H_2SO_4 72h	Noligwa Aggressive H_2SO_4 24h	Noligwa Aggressive H_2SO_4 48h	Noligwa Aggressive H_2SO_4 72h	Moab Aggressive H_2SO_4 24h	Moab Aggressive H_2SO_4 48h	Moab Aggressive H_2SO_4 72h
75.00									
63.00								20.55	
53.00									
45.00									
38.00									
32.00	14.29						15.78		
27.00	15.50					25.93	11.62	4.34	
22.00	21.50		34.73	12.04			7.05		
19.00				11.52	16.73	15.07	3.80	13.55	14.22
16.00	8.40			11.92		16.23	4.10		16.18
13.50	3.67	30.70		7.50	6.33		8.35	14.84	9.26
11.40	3.51		9.46	3.18	5.45	2.85	5.89	8.73	16.88
9.60	2.53			9.30	4.59		6.82	7.03	13.05
8.10	8.07			8.09	7.63	6.75	5.96	10.64	5.12
6.80	7.75	9.22	52.78	4.18	17.33	4.50	8.02	5.82	12.93
5.70	3.28	27.43		9.51	11.42	5.89	6.49	4.87	2.31
4.80	2.19	7.76		8.86	7.16	4.86	4.85	2.74	1.47
4.10	3.25	12.67		4.11	4.75	3.90	2.69	1.46	2.41
3.40	2.23	2.15		4.45	5.52	5.49	2.70	1.92	3.10
2.90	1.21			2.64	3.10	3.65	2.41	1.33	1.28
2.40	0.89	2.12		0.90	2.90	1.97	1.29	0.86	0.96
2.00	0.85	3.21		1.00	1.51	0.75	0.95	0.39	0.30
1.75	0.19	1.13		0.16	1.08	0.46	0.35	0.23	0.35
1.45	0.46	1.22	2.51	0.31	1.30	0.50	0.33	0.28	
1.20	0.10	0.58		0.15	1.15	0.35	0.28	0.23	0.11
1.00	0.05	0.75	0.07	0.11	0.89	0.40	0.08	0.05	
0.87	0.03	0.86	0.44	0.03	0.69	0.11	0.09	0.08	
0.73	0.03	0.20		0.05	0.47	0.12	0.08	0.06	0.07
0.62						0.13			
0.52						0.08			
0.00					0.00				

Table 13.11: Grain size distribution of brannerite particles for Kopanang, Noligwa and Moab Khotsong residue samples for nitric acid digestion tests

Size	Kopanang HNO_3 Digestion	Noligwa HNO_3 Digestion	Moab Khotsong HNO_3 Digestion
75.00			
63.00			
53.00			
45.00			
38.00			
32.00			
27.00		52.05	
22.00			
19.00			
16.00		20.42	
13.50			
11.40			
9.60			
8.10		5.46	
6.80		7.60	
5.70		2.27	
4.80		3.65	
4.10		3.96	
3.40	74.54		77.18
2.90		2.01	
2.40		1.24	
2.00		0.30	22.82
1.75		0.21	
1.45	18.83	0.16	
1.20	2.69	0.30	
1.00		0.30	
0.87		0.06	
0.73	1.75		
0.62	1.31		
0.52	0.88	0.02	
0.00			

Table 13.12: Brannerite associations of the residue samples after leaching at different potentials

	Kopanang Natural Potential	Kopanang 500mV	Kopanang 700mV	Noligwa Natural Potential	Noligwa 500mV	Noligwa 700mV	Moab Khotsong Natural Potential	Moab Khotsong 500mV	Moab Khotsong 700mV
Liberated	7.91	9.49	17.21	33.16	26.69	20.11	42.94	14.03	14.49
Binary Associations	54.74	45.85	37.20	49.45	28.77	49.69	12.69	43.58	55.59
Uranium Minerals	34.86	15.84	0.00	2.79	1.60	25.14	3.28	33.36	3.13
-Uraninite	34.86	15.64	0.00	2.79	1.60	25.14	3.28	33.36	3.13
-U-Phosphate	0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00
-Coffinite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Silicates	17.72	1.74	19.41	17.72	20.75	3.47	5.44	7.62	50.36
-Quartz	1.13	1.52	19.41	16.73	1.42	2.84	4.79	6.09	45.69
-Feldspar	0.16	0.00	0.00	0.99	14.78	0.24	0.21	0.17	3.22
-Chlorite	0.00	0.00	0.00	0.00	4.40	0.00	0.06	0.00	0.00
-Muscovite	16.43	0.08	0.00	0.00	0.15	0.21	0.38	1.28	1.46
-Pyrophyllite	0.00	0.14	0.00	0.00	0.00	0.18	0.00	0.07	0.00
Pyrite	0.71	0.00	0.00	0.24	0.00	0.00	2.32	0.40	0.00
REE-Phoshates	0.00	0.00	12.39	1.70	0.00	0.00	0.17	0.00	0.00
Titanite	0.00	27.70	2.67	26.68	4.49	18.88	1.43	0.50	1.75
Carbon	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.37	0.00
Other	36.31	16.40	2.72	0.31	1.93	2.21	3.34	34.70	3.49
Ternary Associations	37.35	44.66	45.59	17.39	44.53	30.19	44.37	42.39	29.92
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 13.13: Brannerite associations of the residue samples after leaching at different leaching times

	Kopanang Aggressive H_2SO_4 24h	Kopanang Aggressive H_2SO_4 48h	Kopanang Aggressive H_2SO_4 72h	Noligwa Aggressive H_2SO_4 24h	Noligwa Aggressive H_2SO_4 48h	Noligwa Aggressive H_2SO_4 72h	Moab Khotsong Aggressive H_2SO_4 24h	Moab Khotsong Aggressive H_2SO_4 48h	Moab Khotsong Aggressive H_2SO_4 72h
Liberated	19.55	41.56	30.64	36.88	21.87	13.00	27.50	24.02	54.59
Binary Associations	25.97	42.53	46.83	21.98	36.20	60.67	28.33	23.17	31.07
Uranium Minerals	20.99	10.04	0.00	1.78	2.26	10.53	1.79	9.02	2.45
-Uraninite	18.44	10.04	0.00	1.29	2.26	10.53	1.74	9.01	2.45
-U-Phosphate	2.55	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
-Coffinite	0.00	0.00	0.00	0.49	0.00	0.00	0.05	0.00	0.00
Silicates	3.53	10.44	37.37	10.75	10.67	17.13	19.10	10.98	24.37
-Quartz	3.53	10.44	37.37	9.23	10.59	15.94	6.95	9.16	8.06
-Feldspar	0.00	0.00	0.00	0.17	0.00	0.00	1.04	0.08	2.10
-Chlorite	0.00	0.00	0.00	1.15	0.00	0.00	9.47	0.00	0.00
-Muscovite	0.00	0.00	0.00	0.00	0.00	0.00	1.65	1.74	14.22
-Pyrophyllite	0.00	0.00	0.00	0.21	0.07	1.19	0.00	0.00	0.00
Pyrite	0.10	0.00	0.00	0.00	0.00	3.08	0.04	0.31	2.07
REE-Phoshates	0.05	0.84	0.00	0.05	0.00	1.62	0.00	0.07	0.00
Titanite	0.54	18.43	9.46	8.03	20.53	1.93	3.35	1.87	0.00
Carbon	0.41	0.00	0.00	0.04	0.00	0.00	0.00	0.14	0.00
Other	21.34	12.83	0.00	1.33	2.75	26.38	5.84	9.79	4.62
Ternary Associations	54.48	15.90	22.53	41.14	41.93	26.33	44.17	52.81	14.34
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Appendix E – Modelling

14.1 Statistical Modelling

- A copy of the Excel® spreadsheet as well as the Matlab® program and other required files to run this program are included on the attached CD.
- The ranges can be changes under "class" in the Excel® spreadsheet
- Run the program in Matlab®
- To determine the expected range of uranium recovery given the operating parameters use the following function:

  >> treeval (t0, [ore1, ore2, ore3, time, acid, oxidant, temperature])

  For Kopanang ore: ore1=1, ore2=0, ore3=0
  For Noligwa ore: ore1=0, ore2=1, ore3=0
  For Moab Khotsong ore: ore1=0, ore2=0, ore3=1
  Time: hours
  Acid: kg/t
  Oxidant: kg/t
  Temperature: °C

- Matlab® M-file

```
global Xmean Xstd Ymean Ystd VAR_LABELS TARGET_LABELS%#ok
global DEFINE_ADD_LABELS DEFINE_REMOVE_STD %#ok

DEFINE_REMOVE_STD = 1;
DEFINE_ADD_LABELS = 1;

%Import data.xls
data = importdata('Excel spreadsheet.xls');
data = data.data.data;
Results = data(:, 2:end);

%define labels
VAR_LABELS = {'  ' '  ' '  ' '(hrs)' '(kg/t)' '(kg/t)' '(degC)'};
TARGET_LABELS = {'ppm'};

X=Results(:, 1:end-2); %Inputs
```

```
Y=Results(:, end); %Outputs

% LET'S DO REAL CROSS_VALIDATION (Make sure 'utils' folder is on path)
% HOW TO PUT ON PATH?
% >    path(path,genpath('D:\utils'))[Folder utils from CD]
CrossValidationFold = 3; % number of cross-validation folds

% constructing object for cross-validation
CrossValid = crossvalidation(CrossValidationFold);

% preprocess data and other stuff
VAR_NAMES   =   {'Ore1',   'Ore2',   'Ore3',   'Time',   'Acid',   'Oxidant',
'Temperature'};
FEATURES = logical([1 1 1 1 1 1 1]); % 1 - select; 0 - do not select;
TARGERT_VAR = 1;
Xmean=mean(X(:,FEATURES));
Xstd=std(X(:,FEATURES));
Xstd(1:3)=1;
if all(FEATURES(1:3)),
    Xmean(1:3)=0;
    Xstd(1:3)=1;
end
X_without_mean=X(:,FEATURES) - repmat(Xmean, size(X,1), 1);
X_without_mean_divided_by_std=X_without_mean  ./  repmat(Xstd,  size(X,  1),
1);


% initiale cross validation with with pre-processed data
CrossValid = Initialize(CrossValid, X_without_mean_divided_by_std',Y');


%Setup Classification Tree using training data
CONFUSION_MATRICES = cell(CrossValidationFold,1);
t=cell(CrossValidationFold,1);
t0=cell(CrossValidationFold,1);

for fold = 1 : CrossValidationFold
    TrainData = [];
    TrainLabels = [];
    %TestData = [];
    %TestLabels = [];

    % getting current fold
    [TestData TestLabels] = GetFold(CrossValid, fold);

    % concatinating other folds into the training set
    for k = 1:CrossValidationFold
        if(k ~= fold)
            [TrainData   TrainLabels]   =   CatFold(CrossValid,   TrainData,
TrainLabels, k);
        end
    end


    t{fold}=treefit(TrainData', TrainLabels', 'method','class');
    treedisp2(t{fold}, 'names', VAR_NAMES(logical(FEATURES)));
    %Estimate the best tree size by cross validation:
    % Prune tree
    [c,s,ntn] = treetest(t{fold},'resub');
```



```
    [c2,s2,n2,best] = treetest(t{fold},'cross',TrainData',TrainLabels');
    plot(ntn,c,'b-', n2,c2,'r-', n2(best+1),c2(best+1),'mo');
    xlabel('Number of terminal nodes')
    ylabel('Residual variance')
    legend('Resubstitution error','Cross-validation error','Estimated best
tree size')
    best; %#ok
    c2(best+1);
    %Get pruned tree:
    if best==0,
        t0{fold} = treeprune(t{fold},'level',best);
    else
        t0{fold} = treeprune(t{fold},'level',best-1);
    end
    treedisp2(t0{fold},'names',VAR_NAMES(logical(FEATURES)))

    % COMPUTE ERROR ON TEST DATA
    % Determine the CLASSIFICATION STATS on hold-out sample:
    Y_pred =treeval(t0{fold},TestData');
    CONFUSION_MATRICES{fold}=confmat(Y_pred,TestLabels');
end

% view confusion matrices for each hold-out fold and calculate classication
% accuracy
for k=1:CrossValidationFold,
    fprintf(1,'CONFUSION MATRIX for fold #%d\n\n',k)
    disp(CONFUSION_MATRICES{k})
    fprintf(1,'--------------------------\n');
    fprintf(1,'CLASSICATION ACCURACY (fold #%d): %4.2f%%\n',...

k,100*sum(diag(CONFUSION_MATRICES{k}))/sum(sum(CONFUSION_MATRICES{k})));
    fprintf(1,'\n');
    disp(100*diag(CONFUSION_MATRICES{k})'./sum(CONFUSION_MATRICES{k},1));
end
```

14.2 Empirical Modelling

Python® code is included in the attached CD

Appendix F – Publications and Conferences

15.1 Published Paper

- **Minerals Engineering Journal:**

Lottering, M.J., Lorenzen, L., Phala, N.S., Smit J.T., Schalkwyk G.A.C., Mineralogy and uranium leaching response of low grade South African ores, Minerals Engineering, 2007. (copy of paper is attached at the back of thesis)

15.2 Conference Paper

- **Anglo American Metallurgy Symposium:**

Lottering, M., Skudder, J., Lorenzen, L., Phala, N., Smit, J., Schalkwyk, C., Schouwstra, R., Gloy, G., Uranium leaching characteristics of Vaal River ores, Proceedings of the Anglo American Metallurgy Symposium, Johannesburg, November 2006, 625 – 634.

15.3 Conference Presentations

- **Mineral Processing Conference 2006:**

Lottering, M.J., Lorenzen, L., Phala, N.S., Smit J.T., Towards optimisation of uranium leaching.

- **Anglo American Junior Interdivisional Metallurgists' Colloquium 2006:**

Lottering, M.J., Lorenzen, L., Phala, N.S., Smit J.T., Uranium leaching characterists of Vaal River ores

- **Minerals Engineering Conference – Bio and Hydrometallurgy 2007:**

Lottering, M.J., Lorenzen, L., Phala, N.S., Smit J.T., Characterisation of the uranium leaching behaviour of low grade ores.

- **Mineral Processing Conference 2007:**

Lottering, M.J., Lorenzen, L., Development of a diagnostic leaching method for low grade uranium ores.

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Mineralogy and uranium leaching response of low grade South African ores

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Abstract

The efficiency of uranium leaching determines the economic viability of treating low grade uranium deposits, and is quite sensitive to ore characteristics. The interrelationship between mineralogy, mineral liberation and the leaching behaviour of uranium is not well defined. Uraninite's leaching kinetics are well studied, but relatively little leaching research has been conducted for other uranium minerals.

Dissolutions higher than 90% are very difficult to achieve under the normal operating conditions employed for acid leaching of South African ores. In this paper, a mineralogy-leachability explanation is presented to rationalise the difficulty in exceeding 90% dissolution from low grade uranium ores in the Vaal River region (averaging 0.3 kg U_3O_8/t). Based on the findings, further discussed in the paper, it appears that brannerite's intrinsic inertness is responsible for not obtaining optimum recoveries.

It is also shown that for low grade uranium ores in the Witwatersrand context, the real value of uranium leaching could lie in the unlocking of extra gold (0.4–0.6 g/t) by the uranium leaching process that typically precedes cyanide leaching of gold.

Keywords: Hydrometallurgy; Leaching

1. Introduction

Gold deposits in the Vaal River region, South Africa, also contain uranium-bearing minerals. Although the uranium content of the ore is very low by international standards (it averages only 0.3 kg U_3O_8/t), recovering uranium as a by-product of gold production improves the overall processing economics. The benefit is primarily due to the additional gold extraction following the acid pre-treatment of the ore during uranium leaching. However, the current high uranium price and increasing demand due to renewed interest in nuclear power also add significantly to the benefit by making uranium production economic on its own.

Leaching as practiced in South African plants is accomplished by oxidation of the insoluble U^{4+} form to the acid-soluble U^{6+} form in an acidic environment (H_2SO_4), using ferric as an oxidant. To maintain reasonable reaction rates, depleted Fe^{2+} is continually converted to Fe^{3+} using pyrolusite (MnO_2-rich ore), i.e.:

$$UO_2 + 2Fe^{3+} \leftrightarrow UO_2^{2+} + 2Fe^{2+} \quad (1)$$

$$2Fe^{2+} + MnO_2 + 4H^+ \leftrightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O \quad (2)$$

The ferric/ferrous couple serves as an electron transfer catalyst between the solid oxidant, MnO_2, and UO_2. The electrochemical nature of the uranium leaching process means it is confined to a specific Eh–pH window (see Fig. 1). In sulphate systems, U^{6+} exists as $UO_2(SO_4)_n^{2n-2}$ and not the

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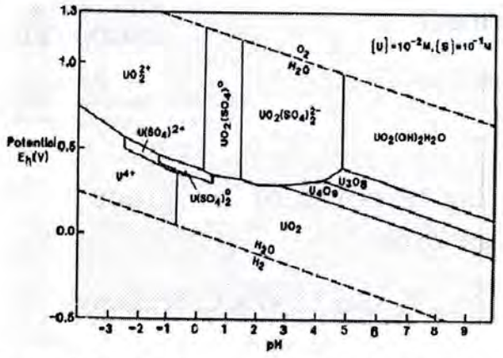

Q1 Fig. 1. Eh/pH diagram of a U–S–H_2O system @ 25 °C (Hayes, 2003).

uncomplexed UO_2^{2+} species. The efficiency of uranium recovery is influenced by the mineralogical characteristics of the ore. In particular, bulk composition affects reagent consumption and ferric generation, while uranium mineral composition and mode of occurrence influences uranium dissolution.

The uranium leaching response of three different ore types from the Vaal River area (further referred to as ores A, B and C) during atmospheric sulphuric acid leaching was investigated. The ores were studied in terms of their leaching responses to variations in acid addition, solid oxidant dosage, and temperature. The ultimate objective was to relate the leach responses to the ore mineralogies.

In the recovering of uranium as a by-product of gold production, two process routes can be considered with respect to gold recovery: (i) forward leaching (direct cyanide leaching of gold) and (ii) reverse leaching (sulphuric acid leaching of uranium followed by cyanide leaching of gold). It is generally accepted that leaching uranium before gold liberates more gold, improving gold recovery. Tests were done to quantify the benefit for the Vaal River ores.

2. Experimental procedure

2.1. Mineralogical analyses

The mineralogical analyses were done on a mineral liberation analyzer (MLA) using polished section of the material investigated. The detailed uranium mineral evaluation uses an automated sparse phase liberation measurement to identify and characterize the grains of the mineral of interest. The particle detected is then analyzed using energy dispersive X-ray analyses.

2.2. Uranium leaching tests

A factorial design setup (2^3 design) was proposed for testing the dependence of the percentage uranium extraction on individual parameters. Key parameters investigated in the uranium leaching experiments were sulphuric acid dosage (9.9 kg/t, 12.8 kg/t, 16.3 kg/t), temperature (40 °C, 50 °C, 60 °C) and MnO_2 addition (2 kg/t, 3 kg/t, 4 kg/t – as 100% MnO_2). The ore samples were rod-milled to a P_{80} of −75 μm. Leaching experiments were carried out in 2 L water-jacketed batch reactors, which were mechanically agitated. The sulphuric acid was added at the beginning of each experiment. A H_2SO_4 solution concentration of 647 g/L was used. Pyrolusite containing 29.3% MnO_2 and 36.5% Fe was used as a solid oxidant and added 1.5 h after the addition of the acid. The absolute dosages were calculated on the basis of a pulp RD of 1.55 and a solids SG of 2.7. Stirring speed was kept constant at 6 rpm.

2.3. Forward and reverse leaching tests

The gold leaching experiments were carried out in 2 L water-jacketed batch reactors which were mechanically agitated. A pulp mixture consisting of 1310 g of the dried milled sample (P_{80} of −75 μm) and 1015 mL water was preheated to 30 °C. The pulp was agitated at 6 rpm to fully suspend the solids. The pH of the pulp was adjusted by addition of small amounts of lime, typical 0.1 g at a time using a spatula. The initial pH was set to ~10.5. Reagent concentrations used were as follows: 40 g/L NaCN and 20 g/L CaOH. Before NaCN was added to the reactor, air was manually sparged. The air sparger was assembled with the baffle and left in the reactor till the end of the test. The test commenced after the addition of 0.65 g NaCN (~347 mg/L CN^-).

The reverse leaching experiments included sulphuric acid leaching of uranium followed by cyanide leaching of gold. The experimental methods are described in Sections 2.2 and 2.3.

3. Results and discussion

3.1. Uranium mineralogy

Like gold, uranium minerals are concentrated in a matrix of pebble-supported conglomerates (Smit, 1984). The bulk mineralogies of the three different ores investigated are fairly similar and consist primarily of quartz (70–80%), with lesser amounts of muscovite (8–11%). From Table 1 it can be seen that samples of ore A are slightly different, and contain less quartz, pyrite and chlorite; and more pyrophyllite, as compared to the other ores.

The uranium concentrations in the different ores also varied within the following ranges: ore A (270–330 ppm), ore B (290–450 ppm) and ore C (390–540 ppm). A detailed uranium mineralogical characterisation of the ore was conducted and the uranium mineral distributions are shown in Table 2.

As expected from earlier studies by Smit (1984), it was found that uraninite as well as brannerite-type minerals ($U_{1-x}Ti_{2+x}O_6$) are jointly responsible for the major portion of uranium carriers in ore from the Witwatersrand basin. Table 2 shows that 80–90% of the uranium in the ores is contained as uraninite, 8–19% as brannerite, and the balance as traces of coffinite and uranium phosphates.

Uraninite dissolves readily in the presence of a lixiviant provided that the required conditions of extraction are met. Brannerite-type minerals, unlike uraninite, are not readily leachable in sulphuric acid and therefore are referred to as refractory. Liebenberg (1955) distinguished between two uraniferous titanates in Witwatersrand ore: uraniferous leucoxene and brannerite which have UO_2:TiO_2 mole ratios of <1 and >1, respectively. One would expect variability in the leaching response amongst brannerite-type minerals, but at this stage of the study different brannerite-types were not investigated. Previous work done by Glatthaar and Duchovny (1979) indicated that Vaal River ores mostly consist of brannerite associated with leucoxene and other titaniferous minerals (termed uraniferous leucoxene) which have a more loosely knit appearance and probably are more readily available for dissolution as compared to brannerite associated with silicates (termed brannerite), which occurs as minute, compact crystals intergrown in the siliceous material. This however, is not indicative that the different types of brannerite minerals will dissolve.

Small amounts of coffinite were present. Coffinite is generally more reactive than brannerite to oxidative sulphuric acid leaching, but less reactive as compared to uraninite. In ore from the Elliot Lake district, which also consists mostly of brannerite and uraninite, secondary coffinite intergrowths are enhancing the overall kinetics of brannerite by accelerating leaching pit formation (Ifill et al., 1996). Further, in the ore samples investigated there were also traces of uranium associated with monazite, which may be inert or reactive, depending on whether uranium is a substitutional impurity or is adsorptively associated with monazite. Ford and Gould (1994) found that the amount of inert uranium is, in absolute terms, fairly similar for all Witwatersrand ores, at about 0.015 kg/t to 0.030 kg/t, suggesting that there is always an amount which is very inert.

The mineralogy investigations focused on uraninite and brannerite, as they form the bulk of the uranium-bearing minerals. Table 3 shows the uranium mineral associations. Most of the unliberated uraninite is associated with silicates, carbon, or has a ternary association. Ore C also has a high percentage uraninite associated with phosphates. Association with carbon is quite low for brannerite.

Uranium grain sizes were found to be very small, with 50% of the particles passing 19.4, 21.3 and 23.2 μm for ore A, ore B and ore C, respectively. The degree of liberation of the uranium-bearing minerals was low (see Table 3), between 11% and 45%, and expectedly increased as particle size decreased. It is important to realize that surface area exposure may be a more useful indicator of leachability of uranium minerals, as opposed to intrinsic liberation. Minerals with exposed surface area are technically leachable as they can be accessed by a lixiviant. Tables 4a and 4b show that between 87% and 93% of the uraninite particles and 71% to 86% of the brannerite particles have more than 10% of their surfaces exposed, and even higher proportions have more than 5% of their surfaces exposed.

Fig. 2 shows the distinction between liberation and surface exposure. It is suggested that the measurement of area exposure of the uranium minerals (especially the fraction with >10% of surface exposed) is a very good indicator of their leachability, because only intrinsic inertness to leaching reagents can cause an exposed mineral to remain unleached.

Uranium minerals seem to have a high percentage surface area exposure, despite poor liberation. This suggests that the breakage of the ore particles occurs near the uranium grains. It needs to be established whether this is due to association with soft gangue components. This means that coarser grinds can be tolerated for uranium leaching than one would suspect from their grain sizes alone.

Table 1
Bulk mineralogy of the three Vaal River ores

Mineral	Formula	Ore A (%)	Ore B (%)	Ore C (%)
Quartz	SiO_2	70.2	73.3	79.8
Muscovite	K–Al-silicate	10.1	11.3	8.2
Chlorite	Mg–Fe–Al-silicate	2.0	3.2	3.6
Pyrophyllite	$Al_4(Si_8O_2)(OH)_4$	9.7	2.5	1.1
Pyrite	FeS_2	1.3	2.5	2.8
Albite	Na–Al-silicate	4.8	5.1	1.9

Table 2
Uranium mineral distribution (area %) of feed samples[a]

Mineral	Formula	Ore A (%)	Ore B (%)	Ore C (%)
Uraninite	UO_2	47.6 (84.9)	42.1 (79.7)	52.8 (89.2)
Brannerite	$(U,Th,Ca)(Ti,Fe)_2O_6$	42.2 (12.9)	49.6 (18.5)	32.3 (7.7)
U-Phosphate	$(U, Cl)PO_4$	3.1 (0.2)	2.5 (0.1)	5.7 (0.4)
Coffinite	$U(SiO)_{41-x}(OH)_{4x}$	7.1 (2.0)	5.8 (1.7)	9.2 (2.7)

Values in brackets represent uranium metal deportment, in %, calculated from ideal mineral uranium contents, assuming spherical shapes to convert area to volume and then to mass of mineral using their ideal densities.
[a] There is no 'standard' U-phosphate mineral, so its uranium concentration was assumed to be the same as that of brannerite and its density that of apatite. Densities used were 10.88, 5.2, 3.19 and 5.44 g/cm³ for uraninite, brannerite, apatite and coffinite, respectively. Uranium contents used were 88.15, 33.54, and 72.63% for uraninite, brannerite, and coffinite, respectively (data mainly from www.webmineral.com).

Table 3
Brannerite and uraninite associations

	Brannerite			Uraninite		
	Ore A	Ore B	Ore C	Ore A	Ore B	Ore C
Binary association	67.8	85.8	67.7	86.0	85.2	86.6
Liberated	11.8	11.1	13.4	30.6	30.9	42.3
Uranium minerals	1.7	7.5	15.7	11.8	7.1	6.5
Silicates	46.8	59.0	28.7	27.4	20.6	24.0
BMS	1.0	2.1	4.1	0.3	0.5	0.7
Oxides	3.6	4.0	4.6	0.1	0.1	0.7
REE-Phosphate	0.0	0.0	0.2	0.0	1.2	8.0
Carbonate	0.0	0.0	0.0	0.0	0.0	0.0
Carbon	2.9	2.1	1.0	15.8	24.8	4.3
Ternary association	32.2	14.2	32.3	14.0	14.8	13.4
Total	100	100	100	100	100	100

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Table 4a
% Uraninite liberation and % of uraninite with 5 and 10% surface exposure

	Ore A (%)	Ore B (%)	Ore C (%)
Liberated	30.6	30.9	42.3
Middlings	26.1	31.6	31.2
Locked	43.3	37.5	26.5
Total	100	100	100
5% Surface exposure	96.4	96.4	98.3
10% Surface exposure	88.9	87.4	93.2

Table 4b
% Brannerite liberation and % of brannerite with 5 and 10% surface exposure

	Ore A (%)	Ore B (%)	Ore C (%)
Liberated	11.8	11.1	13.4
Middlings	38.7	53.4	29.6
Locked	49.5	35.5	57.0
Total	100	100	100
5% Surface exposure	93.9	94.2	87.8
10% Surface exposure	79.3	86.1	71.3

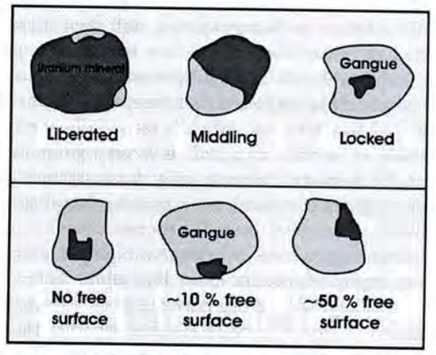

Fig. 2. Distinction between liberation and surface exposure.

3.2. Uranium dissolution

Standard leaching tests done showed that the maximum uranium recovery within the chosen parameter space never exceeded 90%, for a 24 h leaching period. A summary is presented in Tables 5a, 5b and 5c. The independent estimate of error (based on centre-point triplicates; temp: 50 °C, MnO_2: 3 kg/t, H_2SO_4: 12.8 kg/t) determined for ore A, ore B and ore C for 24 h are 1.5, 0.4 and 2% points, respectively.

The dissolution curve as well as the potential profile, for the aggressive leaching conditions, over a 24 h period is presented in Figs. 3 and 4. Note that the increase in potential after 1.5 h is due to the addition of the oxidant.

Acid dosage was found to have the greatest effect on uranium dissolution. The insensitivity of the uranium dissolution to temperature suggested mass-transfer (either internal or external) control, but since there are a lot of variables their interaction has to be understood before making definite conclusions, especially because the temperature range tested is relatively narrow (20 °C).

There can be various reasons for not achieving dissolutions higher than 90%. Since acid concentration is the most influential parameter, and to ensure that the uranium dissolution reaction was not acid limited, acid dosage was increased to 25 kg/t. However, there was no significant improvement beyond 90% (see Table 6).

Although there is still uncertainty regarding the dissolution of brannerite, some of the brannerite must dissolve in order to achieve ~90% total uranium dissolution, because it cannot be accounted for by uraninite dissolution alone (refer to Table 2). Mineralogical analysis (Table 7) showed that uraninite has been mostly dissolved (only small amounts remained in the residue) and that the largest fraction of unleached uranium present in the residue exists as brannerite.

Investigating the liberation and surface exposure of the residue brannerite, it seems that brannerite is exposed to the lixiviant (Table 8). Therefore, neither liberation nor surface area exposure is expected to influence optimum uranium recovery.

Table 5a
Percentage uranium dissolution after 24 h for ore A. Acid consumption is included in kg/t in brackets

	High temp (60 °C)	High temp (60 °C)	Low temp (40 °C)	Low temp (40 °C)
High Acid (16.3 kg/t)	90.3 (11.2)	86.6 (13.3)	85.2 (12.8)	87.4 (10.8)
Low Acid (9.9 kg/t)	63.8 (9.2)	68.3 (8.3)	63.8 (8.7)	68.0 (8.0)
	High MnO_2(4 kg/t)	Low MnO_2(2 kg/t)	High MnO_2(4 kg/t)	Low MnO_2(2 kg/t)

Table 5b
Percentage uranium dissolution after 24 h for ore B. Acid consumption is included in kg/t in brackets

	High temp (60 °C)	High temp (60 °C)	Low temp (40 °C)	Low temp (40 °C)
High Acid (16.3 kg/t)	83.5 (14.8)	86.2 (14.2)	86.7 (11.9)	83.1 (11.6)
Low Acid (9.9 kg/t)	71.8 (9.6)	73.7 (9.2)	76.5 (9.0)	69.8 (8.6)
	High MnO_2(4 kg/t)	Low MnO_2(2 kg/t)	High MnO_2(4 kg/t)	Low MnO_2(2 kg/t)

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Table 5c
Percentage uranium dissolution after 24 h for ore C. Acid consumption is included in kg/t in brackets

	High temp (60 °C)	High temp (60 °C)	Low temp (40 °C)	Low temp (40 °C)
High Acid (16.3 kg/t)	80.5 (15.9)	66.7 (15.4)	80.0 (13.7)	79.8 (12.6)
Low Acid (9.9 kg/t)	67.9 (9.6)	70.9 (9.4)	70.3 (9.3)	70.9 (8.9)
	High MnO_2 (4 kg/t)	Low MnO_2 (2 kg/t)	High MnO_2 (4 kg/t)	Low MnO_2 (2 kg/t)

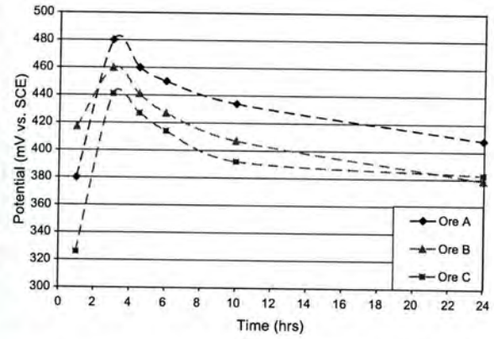

Fig. 3. Potential profile for aggressive leaching conditions (H_2SO_4: 16.3 kg/t, MnO_2: 4 kg/t, temp: 60 °C).

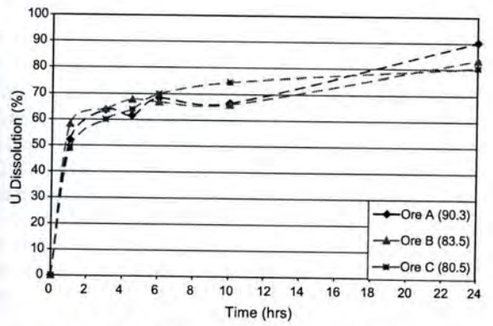

Fig. 4. Uranium dissolution versus time for aggressive leaching conditions (H_2SO_4: 16.3 kg/t, MnO_2: 4 kg/t, temp: 60 °C) End dissolutions are included in brackets.

Table 6
Comparison of uranium dissolutions between aggressive (Acid: 16.3 kg/t) and most aggressive (Acid: 25 kg/t) conditions at 60 °C and MnO_2 addition of 4 kg/t

Ore type	Uranium dissolution at aggressive conditions (%)	Uranium dissolution at most aggressive conditions (%)
Ore A	90.3 (11.2 kg/t)	89.0 (18.6 kg/t)
Ore B	83.5 (14.8 kg/t)	85.5 (22.2 kg/t)
Ore C	80.5 (15.9 kg/t)	84.0 (22.5 kg/t)

The acid consumptions are included in brackets in kg/t.

The fact that the largest fraction of unleached uranium present in the residue exists as brannerite (Table 7), which is in fact exposed to the lixiviant (Table 8), is an indication of the slow reaction kinetics of brannerite. In a theoretical study to determine if brannerite is intrinsically inert or thermodynamically limited it was found that it maybe possible to extend brannerite dissolution by employing extreme leaching conditions (e.g. pressure leaching at high potentials and temperature). It complies with the findings by Zhang et al. (2003) that the rate of uranium release from brannerite is an order of magnitude lower than the release from uraninite.

In the experiments, a simple doubling of residence time to 48 h and use of nitric acid did not show any improvement in overall uranium dissolution and therefore, a more in-depth study is necessary to understand the leaching kinetics of brannerite. It must be noted that these dissolutions are actually quite high in absolute terms, considering that the feed grade is typically what would report to the residue in most international uranium mines.

Table 7
Uranium mineral distribution (%) in the residue samples of the aggressive leaching tests H_2SO_4: 16.3 kg/t, MnO_2: 4 kg/t, temp: 60 °C for all three ores

Mineral	Formula	Ore A (%)	Ore B (%)	Ore C (%)
Uraninite	UO_2	9.5	1.0	10.2
Brannerite	$(U,Th,Ca)(Ti,Fe)_2O_6$	69.9	91.2	73.6
U-Phosphate	$(U, Cl)PO_4$	15.8	7.3	10.4
Coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$	4.8	0.5	5.8

Table 8
% Brannerite liberation and % of brannerite with 5 and 10% surface exposure for residue samples of the aggressive leaching tests H_2SO_4: 16.3 kg/t, MnO_2: 4 kg/t, temp: 60 °C for all three ores

Brannerite	Ore A (%)	Ore B (%)	Ore C (%)
Liberated	26.5	11.9	40.6
Free surface >5%	88.9	92.3	89.9
Free surface >10%	86.2	85.2	85.7

3.3. Reagent consumption

Reagent consumption varied for the three ores. The results indicated that ore A consumes less acid, as compared to the others. Comparing the residue analysis to the bulk mineralogy, reasons for different acid consumptions can be established.

Quartz, muscovite, pyrophyllite and albite are found not to be major acid consumers, while chlorite is the most important acid consumer (see Table 9).

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Table 9
Residue bulk mineralogies of the three ores for most aggressive leaching conditions H_2SO_4: 25 kg/t, MnO_2: 4 kg/t, temp: 60 °C

	Ore A		Ore B		Ore C	
	Bulk (%)	Residue (%)	Bulk (%)	Residue (%)	Bulk (%)	Residue (%)
Quartz	70.2	70.2	73.3	73.3	79.8	79.8
Muscovite	10.1	13.9	11.3	12.4	8.2	12.9
Chlorite	2.0	0.6	3.2	0.8	3.6	1.4
Pyrophylite	9.7	11.8	2.5	2.8	1.1	2.2
Pyrite	1.3	0.6	2.5	1.1	2.8	1.5
Carbonates	0.1	0.0	0.2	0.0	0.1	0.0
Albite	4.8	7.6	5.1	6.1	1.9	5.2
K-Feldspar	0.8	3.4	0.4	2.7	1.3	2.1
REE-phosphates	0.1	0.0	0.2	0.0	0.1	0.0
Other silicates	0.1	1.2	0.2	2.4	0.3	2.7
Other oxides	0.4	0.6	0.4	0.4	0.2	0.5
Copper	0.0	0.0	0.0	0.0	0.1	0.0
Carbon	0.2	0.3	0.5	0.6	0.3	0.5

Note that the residue values were re-normalized to quartz (not expected to dissolve) to compare feed and residue bulk mineralogies.

The lower chlorite concentration in ore A is thought to be partly responsible for the lower acid consumption (refer to Tables 5 and 6) as well as lower uranium concentrations. Although chlorite is an acid consumer, it is also an iron producer providing the necessary iron for uranium leaching before the addition of a solid oxidant. The idealized chlorite reaction is presented in reaction (3).

$$Mg_2Fe_2Al_{3.3}Si_{2.5}O_{10}(OH)_8 + 4H_2SO_4 \rightarrow 2Mg^{2+} + 1.7Fe^{2+} + 0.3Fe^{3+} + 3.3Al^{3+} + 4SO_4^{2-} + 2.5SiO_4^{2-} + 8H_2O \quad (3)$$

For oxidant requirements, pyrolusite is mostly used in the mining industry, since it is inexpensive. MnO_2 has the thermodynamic potential to oxidize U^{4+}, but since it is kinetically difficult for a solid to oxidize another solid, manganese dioxide works via iron (Fe^{2+}). Before introducing additional iron to the system it is important to establish if the soluble iron content in the ore is sufficient or not. In the absence of interfering ions, iron from chlorite will result in an initial Eh of ~414 mV before addition of pyrolusite and hence initiate dissolution of fast leaching uranium fractions. Pyrite on the contrary consumes Fe^{3+} but generates Fe^{2+} as well as H_2SO_4 (see reaction (4)).

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

Analysis of the Fe:U mole ratio indicated sufficient iron being available throughout the leaching process for the uranium leaching reactions.

3.4. Effect of reverse leaching on gold recovery

Gold is generally insoluble in acid solutions in the absence of a suitable lixiviant. Therefore, through acid pre-treatment it is possible to dissolve gangue minerals to liberate gold without actually dissolving the gold itself. Results obtained for forward leaching (direct cyanide leaching of gold) and reverse leaching (sulphuric acid leaching of uranium followed by cyanide leaching of gold) are presented in Table 10. (Tests were done in duplicate.)

Table 10
Gold residue grades for the forward and reverse leach method for 8 and 24 h

	Au residue grade (g/t)						
	Forward leach			Reverse leach			Δ
	Au Grade	8 h	24 h	Au Grade	8 h	24 h	24 h
Ore A: Test 1	7.99	0.77	0.48	7.66	0.19	0.12	0.36
Test 2	8.29	0.71	0.64	8.48	0.28	0.13	0.51
Ore B: Test 1	11.60	1.00	0.69	9.71	0.32	0.27	0.42
Test 2	10.60	0.86	0.68	7.96	0.36	0.23	0.45
Ore C: Test 1	12.60	0.97	0.93	12.70	0.67	0.31	0.62
Test 2	11.70	0.84	0.71	14.00	0.38	0.28	0.43

A gold recovery benefit of between 0.4 and 0.6 g/t was measured for the Vaal River ores. This improves gold recovery by 3–4% points to a total gold recovery of ~98% which have a definite monetary benefit.

Future work includes complete mass balances as well as a detailed comparative study of the kinetics of electrochemical dissolution of uraninite and brannerite minerals, to help establish optimum operating strategies for maximum uranium and gold dissolution from Witwatersrand ore.

4. Conclusions

It was found that it is very difficult to achieve uranium dissolutions higher than 90% for the Vaal River ores under conventional uranium leaching conditions. The predominant uranium mineral in the residue samples is brannerite, which is highly exposed, and some of it even fully liberated. The dissolutions achieved are in the region of the uranium fraction associated with uraninite in the feed. The fraction of brannerite with free surface exposure >10% in the residue samples varies between ~58% and 92%, as in the feed samples. Therefore, brannerite intrinsically reacts very slowly. Under the normal operating window, i.e. not considering uneconomical leaching conditions, ~90% dissolution will be a maximum. Aggressive leaching conditions as defined in this paper are thought to be suitable for extracting maximum value out of an atmospheric leach set-up. If ~100% extraction is desired, more extreme conditions (probably pressure leaching) will be necessary. The leaching of uranium before gold results in improvements in gold recovery by 3–4% points to a total gold recovery of 98%.

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